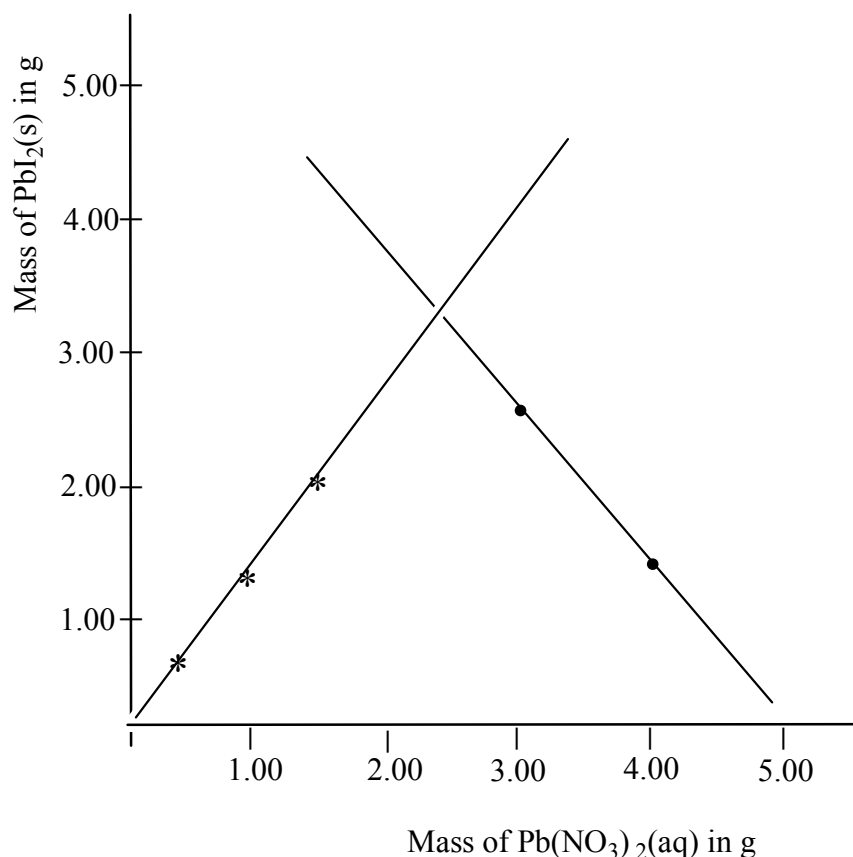


Problem 14: Lead iodide

1. The graph obtained is one of two straight lines, meeting at a peak of about 2.50 g $\text{Pb}(\text{NO}_3)_2$.

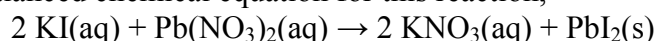
Data according to the reaction
 $2 \text{KI}(\text{aq}) + \text{Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow 2 \text{KNO}_3(\text{aq}) + \text{PbI}_2(\text{s})$

Mass of $\text{Pb}(\text{NO}_3)_2$ (g)	Mass of PbI_2 (g)
0.500	0,696
1.000	1.392
1.500	2.088
4.000 (1.000 g KI)	1.389
3.000 (2.000 g KI)	2,778



2. The total quantity of reactant is limited to 5.000 g. If either reactant is in excess, the amount in excess will be “wasted”, because it cannot be used to form product. Thus, we obtain the maximum amount of product when neither reactant is in excess; there is a stoichiometric amount of each.

The balanced chemical equation for this reaction,



shows that stoichiometric quantities are two moles of KI (166.00 g/mol) for each mole of $\text{Pb}(\text{NO}_3)_2$ (331.21 g/mol). If we have 5.000 g total, we can let the mass of KI equal x g, so that the mass of $\text{Pb}(\text{NO}_3)_2 = (5.000 - x)$ g. Then we have

$$\text{amount KI} = x \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = \frac{x}{166.00}$$

$$\text{amount Pb}(\text{NO}_3)_2 = (5.000 - x) \text{ g Pb}(\text{NO}_3)_2 \times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{331.21 \text{ g Pb}(\text{NO}_3)_2} = \frac{5.000 - x}{331.21}$$

At the point of stoichiometric balance, amount KI = $2 \times$ amount $\text{Pb}(\text{NO}_3)_2$

$$\frac{x}{166.00} = 2 \times \frac{5.000 - x}{331.21} \quad \text{or} \quad 331.21x = 10.00 \times 166.00 - 332.00x$$

$$x = \frac{1660.0}{331.21 + 332.00} = 2,503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = 0.01508 \text{ mol KI}$$

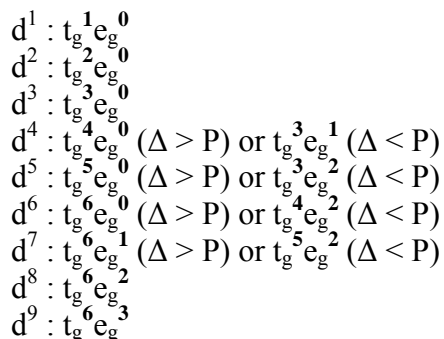
$$5.000 - x = 2.497 \text{ g Pb}(\text{NO}_3)_2 \times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{331.21 \text{ g Pb}(\text{NO}_3)_2} = 0.007539 \text{ mol Pb}(\text{NO}_3)_2$$

To determine the proportions precisely, we use the balanced chemical equation.

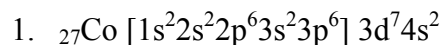
$$\text{maximum PbI}_2 \text{ mass} = 2.503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} \times \frac{1 \text{ mol PbI}_2}{2 \text{ mol KI}} \times \frac{461.0 \text{ g PbI}_2}{1 \text{ mol PbI}_2} =$$

3.476 g PbI₂

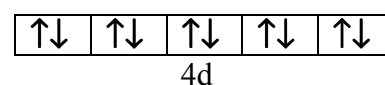
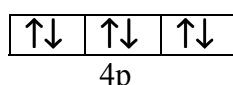
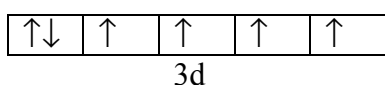
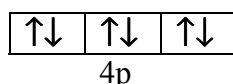
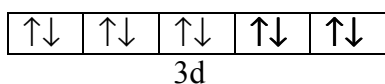
Problem 15: Octahedral complexes



Problem 16: Isomerism in Inorganic Chemistry

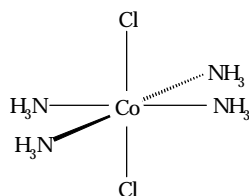


2. dative covalent by the ligand into an empty metal orbital. $d^2 sp^3$ hybridization

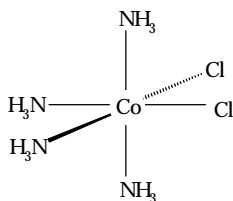


outer sphere paramagnetic complex

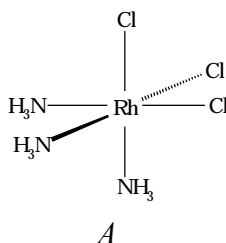
3. *trans*



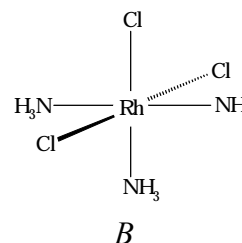
cis



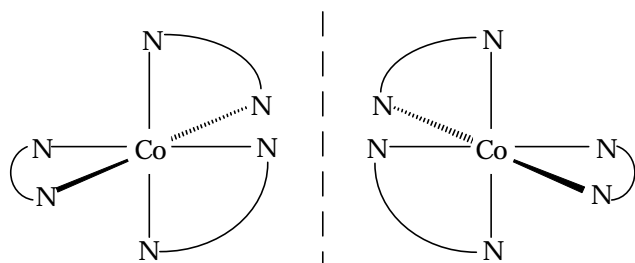
4. *fac*



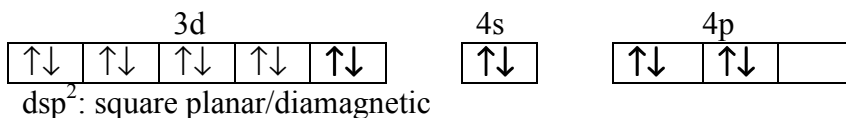
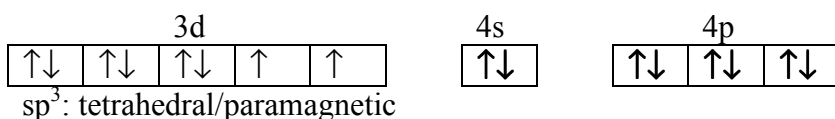
mer



5. 2 enantiomers $\pm \text{Co}(\text{en})_3^{3+}$



Problem 17: Tetrahedral and square complexes



Problem 18: Copper enzyme

- Cu: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹, Cu(I): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰,
 a. Cu(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹
- Oxidised PC
- $A = \epsilon \cdot c \cdot l \Rightarrow c = 0.700 / (4500 \times 1) = 1.56 \times 10^{-4} \text{ mol dm}^{-3}$. 5 cm³ of the solution contain $1.56 \times 10^{-4} \times 5 \times 10^{-3} \times 10500 \times 1000 = 8.2 \text{ mg PC}$. #Cu atoms = $1.56 \times 10^{-4} \times 5 \times 10^{-3} \times 6.0221 \times 10^{23} = 4.7 \times 10^{17}$
- Electronic configurations :
 Zn(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰, Cd(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶ 4d¹⁰,
 Co(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁷, Ni(II): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸. Redox inactive are the Zn(II) and Cd(II) reconstituted Blue Copper Proteins.

Problem 19: Palladium nanoclusters

$$1. N = \frac{N_o \cdot \rho \cdot V}{AtomicWeight} = 307 \text{ Pd(0) atoms per nanocluster}$$

$$V = \text{the volume of a nanocluster} = \frac{4}{3} \pi \left(\frac{D}{2} \right)^3$$

According to the equation $y=10n^2+2$, the number of Pd(0) atoms in a 4 full-shells nanocluster is $N = 1+12+42+92+162 = 309$, hence it is a full shell cluster.

2. From Fig. 4 the H₂ uptake is $\Delta P_{H_2} = 4.15 - 2.05 = 2.10 \text{ atm}$ in 184 min.

$$\Delta P_{H_2} V = \Delta n_{H_2} RT, \text{ hence } \Delta n_{H_2} = 0.029 \text{ mol where } V = 400-55=345 \text{ cm}^3$$

$$\text{Initially } n_{C_6H_{12}} = \frac{V\rho}{M} = \frac{5 \text{ cm}^3 \times 0.81 \text{ g cm}^{-3}}{(6 \times 12.0107 + 12 \times 1.00794) \text{ g mol}^{-1}} = 0.048 \text{ mol}$$

$$(i) \text{ Conversion} = \frac{\text{reacted moles}}{\text{initial moles}} = \frac{0.029}{0.048} = 0.60 = 60\%$$

$$(ii) \text{ The catalytically active Pd(0) atoms are } \frac{162}{309} = 0.524 = 52.4\% \text{ of the total Pd(0)}$$

$$\text{amount. So: TON} = \frac{n_{H_2}}{n_{Pd}} = \frac{0.029 \text{ mol}}{0.524 \times 50 \times 10^{-6} \text{ mol}} = 1106 \text{ and}$$

$$\text{TOF} = \frac{\text{TON}}{t} = \frac{1106}{184 \text{ min}} = 6.0 \text{ min}^{-1}$$

3. The spectral regions (δ / ppm) and the respective relative integrals in the ¹H-NMR spectrum of hex-1-ene (Fig. 5a and Table) are assigned as follows:

	1	2	3	4	5
CH ₃ (CH ₂) ₂ CH ₂ CH=CH ₂	0.88-0.96 (3)	1.15-1.32 (4)	1.99-2.08 (2)	5.65-5.79 (1)	4.85-4.98 (2)

The integral ratios of the second $^1\text{H-NMR}$ spectrum (Fig. 5b and Table) suggest that both hex-1-ene and hexane are present. The differences in the integral values of the spectral regions 0.88-0.96 ppm and 1.12-1.37 ppm must be due to the presence of hexane. The relative integrals of second spectrum are converted as shown in the table below:

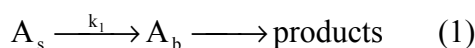
	δ / ppm	relative integral
Solution of the reaction (Fig. 5b)	0.88-0.96	3+6
	1.12-1.37	4+8
	1.99-2.08	2
	4.85-4.98	2
	5.65-5.79	1

So, the spectral regions (δ / ppm) and the respective relative integrals in the $^1\text{H-NMR}$ spectrum corresponding to hexane are assigned as follows:

1' 2' 1'	1'	2'
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	0.88-0.96 (6)	1.15-1.32 (8)

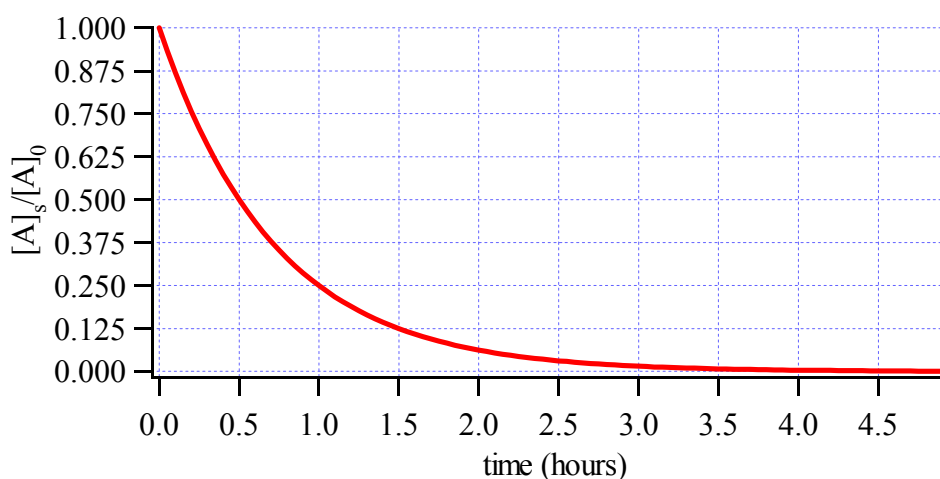
Finally, comparing the integral values per proton for the hex-1-ene and hexane the % conversion of hex-1-ene to hexane, after 30 min is 50%

Problem 20: Drug kinetics



$$-\frac{d[A]_s}{dt} = k_1[A]_s \quad (2)$$

Integration of Eq. 2 gives $[A]_s = [A]_0 \exp(-k_1 t)$, where $[A]_0$ the concentration of the drug in the stomach at zero time.



$\frac{[A]_0 - [A]_s}{[A]_0} = 0.75 \Rightarrow \frac{[A]_s}{[A]_0} = 0.25 = \left(\frac{1}{2}\right)^2$ Since $\frac{1}{4}$ of the initial amount remains after one hour, $(\frac{1}{4})^2 = \frac{1}{16} = 0.0625$ will remain after 2 hours, which corresponds to 4 half lives. That is 6.25% of $[A]_s$ is left.

Problem 21: Br₂ + CH₄ reaction mechanism

1 The rate of formation of CH₃Br is given by the equation:

$$v = + \frac{d[\text{CH}_3\text{Br}]}{dt} = k_3[\text{CH}_3][\text{Br}_2] \quad (1)$$

The “steady state” approximations for CH₃ and Br are given by the equations:

$$\frac{d[\text{CH}_3]}{dt} = k_2[\text{Br}][\text{CH}_4] - [\text{CH}_3](k_3[\text{Br}_2] + k_4[\text{HBr}]) = 0 \quad (2)$$

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2][\text{M}] - k_2[\text{Br}][\text{CH}_4] + [\text{CH}_3](k_3[\text{Br}_2] + k_4[\text{HBr}]) - 2k_5[\text{Br}]^2[\text{M}] = 0 \quad (3)$$

From equation (2):

$$[\text{CH}_3]_{\text{st}} = \frac{k_2[\text{Br}][\text{CH}_4]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad (4)$$

From equations (3) and (4):

$$[\text{Br}]_{\text{st}} = \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{\frac{1}{2}} \quad (5)$$

By combining equations (1), (4) and (5) the expression for the rate of formation of CH₃Br as a function of the concentrations of the stable species that are involved in the reaction is given by equation (6):

$$v = \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} k_2 \cdot \frac{[\text{Br}_2]^{\frac{1}{2}} [\text{CH}_4]}{\frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]} + 1} \quad (6)$$

2

Start of the reaction	II
Steady state condition	I
Near to the end of the reaction	III

3

Start of the reaction	[Br ₂] >> [HBr] and since k ₃ ≈ k ₄ : k ₃ [Br ₂] >> k ₄ [HBr], so k ₄ [HBr] / k ₃ [Br ₂] << 1
Steady state condition	-
Near to the end of the reaction	[Br ₂] << [HBr] and since k ₃ ≈ k ₄ : k ₃ [Br ₂] << k ₄ [HBr], so k ₄ [HBr] / k ₃ [Br ₂] >> 1