Ministère de l'Enseignement Supérieur et de la Recherche Scientifique
Université Dr. Tahar Moulay de Saida
Faculté de Technologie

Département de Génie des Procédés

HANDOUT
OF STRUCTURE OF MATTER

Présenté par :

Dr. Bouchentouf Salim

Maître de conférences « A » en Chimie

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HANDOUT
OF STRUCTURE OF MATTER

FOR FIRST-YEAR COMMON CORE PROGRAMS IN SCIENCE AND TECHNOLOGY,
MATERIAL SCIENCES, ENGINEERING, AND LIFE SCIENCES

Dr.Hab. BOUCHENTOUF Salim

Doctor Moulay Tahar University of Saïda

salim.bouchentouf@univ-saida.dz
bouchentouf.salim@yahoo.fr

Preamble of the handout

The study of the "Structure of Matter" module holds paramount importance in the field of science and technology. This module offers a comprehensive understanding of the fundamental building blocks of the universe, providing invaluable insights into the very fabric of our physical world.

One of the primary benefits of delving into the Structure of Matter lies in its ability to unravel the mysteries of the atomic and molecular realms. By exploring the inner workings of atoms and molecules, scientists and researchers gain profound insights into chemical reactions, material properties, and the behavior of substances under various conditions.This knowledge forms the bedrock of chemistry and physics, enabling advancements in fields such as material science, nanotechnology, and pharmaceuticals.

Furthermore, the Structure of Matter module plays a pivotal role in fostering innovation. It serves as a cornerstone for developing cutting-edge technologies and engineering solutions. Understanding the arrangement and behavior of particles at the atomic level allows us to design new materials with tailored properties, improving the efficiency and functionality of countless products, from electronics to healthcare devices.

The present tutorial booklet for the "Structure of Matter" module is intended for students in their first years of the common core programs in Science and Technology, as well as Material Sciences. It may also prove valuable to students in the fields of biology and pharmacy. Additionally, it can cater to the needs of students in preparatory schools and other disciplines requiring fundamental knowledge in general chemistry.

The exercises and problems covered here have been carefully selected from the tutorial sheets provided in various universities in Western Algeria and from various textbooks. The manual is divided into several chapters, primarily based on the curriculum of the "Structure of Matter" module established by the National Pedagogical Committee of the Algerian Ministry of Higher Education and Scientific Research.

Each set of exercises and problems is preceded by a brief review of the course and important concepts. Some necessary data and constants required for solving the exercises are provided in the appendix. The choice and quantity of exercises per chapter are based on both the objective-based and competency-based approaches, aiming to meet the needs of the learner.

Contents

Chapter 1

Fundamental Concepts

1.1 Important Concepts and Course Review

♣ Avogadro's number ($\mathcal{N}$) is the constant 6.023×10^{23}, representing the number of atoms in a mass (in g) of a pure substance corresponding to its relative atomic mass, or the number of molecules in a mass (in g) of a pure substance corresponding to its molecular mass.

♠ The unit of atomic mass is defined as one-twelfth the mass of a carbon atom $^{12}_{6}$C: $1\ \text{u} = \dfrac{1}{\mathcal{N}}\text{g} = 1.6606 \times 10^{-27}$ kg.

The mole is the amount of substance containing 6.023×10^{23} entities (molecules, atoms, ions). Its symbol is mol, and the number of moles is represented by the letter n.

♣ The mass of one mole of atoms or molecules, known as molar mass (M), is the relative atomic or molecular mass expressed in **g/mol**.

Hence, the mass of a substance (in g) is equal to the quantity of substance (in mol) multiplied by the molar mass (in g/mol).

$$m(g) = n(mol) \times M(g/mol)$$

where
– m is the mass of the substance (in g),
– n is the number of moles (in mol),
– M is the molar mass (in g/mol).

♣ **Gas Laws**
● **Boyle-Mariotte Law**:

$$\text{P.V} = \text{constant.}$$

where:
– P = gas pressure (Pa)
– V = gas volume (m^3)

● **Charles's Law**:

$$\frac{V}{T} = constant'$$

where:
– V = gas volume (m^3)
– T = absolute temperature of the gas (K); T = t + 273.15
– t = temperature in °C

♠ **Ideal Gas Law**:

$$P.V = n \times R \times T$$

where:
– P = gas pressure (Pa)
– V = gas volume (m^3)
– n = number of moles of gas (mol)
– R is the gas constant = 8.314 m^3 . Pa . K^{-1} . mol^{-1}
– T = absolute temperature of the gas (K); T = t + 273 °C

★ The molar gas volume is denoted as V$_m$. At 0°C and at a pressure of 1 atmosphere, the molar gas volume is 22.4 l/mol.
● A temperature of 0°C and a pressure of 1 atmosphere are now referred to Normal Conditions of Temperature and Pressure (NTP).
● A temperature of 25°C and a pressure of 1 atmosphere are now referred to Standard Conditions of Temperature and Pressure (STP).
♠ The density or relative density of a substance is the ratio of its density to the density of a reference substance. For liquids and solids, the reference substance is pure water at 4°C.
For gases or vapors, the reference gas is air, at the same temperature and pressure.
Density, denoted as d, is expressed as:
$d = \dfrac{\rho_{substance}}{\rho_{ref}}$
where: $\rho_{substance}$ is the density of the substance (Volumic mass), and ρ_{ref} is the density of the reference substance (Volumic mass).

♣ **Concentrations**
● Mass concentration: Mass concentration = m (g)/V (L)
● Molar concentration (molarity): Molar concentration (C) = n (mol)/V (L)
● Normality (N) expresses the number of gram equivalents of solute per liter of solution. The gram equivalent is the quantity of substance containing one mole of the considered particles (H$^+$, e$^-$, etc.).
Normality N = Z × C
where C is the molar concentration and Z is the number of H$^+$, e$^-$, etc.

• Molality: The molality of the solute (μ) is the ratio of the number of moles of solute to the mass (in g) of the solvent, multiplied by 1000.
or:
The molality of the solute is the ratio of the number of moles of solute to the mass (in kg) of the solvent.

$$\mu_{sol} = \frac{n_{sol} \times 1000}{m_{sol}}$$

where: n_{sol} is the number of moles of the solute and m_{sol} is the mass of the solvent.

• Mole fraction: The mole fraction of the solute is the ratio of the number of moles of solute to the total number of moles in the solution (solvent + solute).

$$X_{sol} = \frac{n_{sol}}{n_{sol} + n_{solvent}}$$

where: X_{sol} is the mole fraction of the solute, n_{sol} is the number of moles of the solute, and $n_{solvent}$ is the number of moles of the solvent.

• Mass fraction: The mass fraction X_i of component i is the ratio of the mass m_i of that component to the total mass m_{total} of the mixture.

$$X_i = \frac{m_i}{m_{total}}$$

★ By multiplying by 100, you obtain the mass percentage.

♣ **Raoult's Laws**

• **Ebulliometry (1$^{\text{st}}$ Raoult's Law)**

$\Delta T_e = K_e \times C_m$

where: K_e: ebulliometric constant, C_m: molality of the solution.

• **Cryometry (2$^{\text{nd}}$ Raoult's Law)**

$$\Delta T_f = K_f \times \frac{m_{solute}}{m_{solute} \times m_{solvent}}$$

K_f: cryometric constant of the solvent.

Raoult's law is valid only for dilute and volatile solutions.

Normal Conditions of Temperature and Pressure (NTP):
- Temperature: 0°C (273.15 K)
- Pressure: 1 atm (atmosphere) or 101.325 kPa (kilopascals)
- Molar volume: 22.414 L/mol (under these conditions)
- Mainly used in chemistry, particularly for calculations involving chemical reactions.

Standard Conditions of Temperature and Pressure (STP):
- Temperature: 25°C (298.15 K)
- Pressure: 1 atm (atmosphere) or 101.325 kPa (kilopascals)
- Molar volume: 24.465 L/mol (under these conditions)
- Often used in physics and engineering, particularly in calculations involving ideal gases and materials science.

1.2 Exercise Statements

Exercise 01

1. Why is the atomic number of a chemical element defined by the number of protons and not by the number of electrons?

2. Complete the following sentences:

   - 12 u.m.a is the mass of ....
   - 12 g is the mass of ....
   - One mole of electrons contains ....

Exercise 02

Which of the following samples contains the most iron?

1. 0.2 moles of Fe_2SO_4

2. 20 g of iron

3. 2.5×10^{23} iron atoms

Data: $M_{Fe} = 56$ g/mol, $M_S = 32$ g/mol, Avogadro's number $\mathscr{N} = 6.023 \times 10^{23}$

Exercise 03

In a sample of copper oxide CuO with a mass m = 1.59 g, how many:

- moles of CuO are there?

- moles of Cu and moles of O?

- molecules of CuO?

- grams of Cu and grams of O?

- atoms of Cu and atoms of O?

Data: $M_{Cu} = 63.54$ g/mol, $M_O = 16$ g/mol

Exercise 04

Balance and indicate, for each of the following chemical reactions, the number of phases (homogeneous, heterogeneous) and the simple or compound substances:

- $.......Fe_{(s)} + ...H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + ...H_{2(g)}$

- $......H_{2(g)} + ...O_{2(g)}.....+ S_s \rightarrow .....H_2SO_{4(l)}$

Calculate the densities for the gases relative to air under normal temperature and pressure conditions, knowing that the density of air $\rho = 1.293 \times 10^{-3}$ g/cm^3.

Exercise 05

A concentrated solution of hydrochloric acid HCl with a volume of 20 cm^3 containing 8.36 g of pure HCl has a density of 1.18 g/cm^3. Determine for this solution:

- Molarity.

- Normality.

- Molality.

- Mass percentage of HCl.

- Molar and mass fractions of HCl in the solution.

Exercise 06

1) Weigh 10 g of NaCl using a balance. What is the quantity of moles of NaCl in the measured mass?

2) Place the 10 g of NaCl in a 250 ml flask. What is the molar concentration of the solution? <u>Given</u>: $M_{NaCl} = 58.5$ g/mol.

Exercise 07

We want to prepare 250 ml of a 2.5 mol/l copper sulfate CuSO$_4$ solution. Given: M Cu = 63.55 g/mol, M S = 32 g/mol, and M O = 16 g/mol.

1) What mass of CuSO$_4$ should be weighed?

2) Pipette 10 ml of this solution and place it in a 250 ml volumetric flask. What is the concentration of the resulting solution?

Exercise 08

5 g of FeCl$_3$ is dissolved in a 250 ml volumetric flask. Given: M Fe = 55.9 g/mol and M Cl = 35.5 g/mol.

- Calculate the molar mass of FeCl$_3$.

- What is the molar concentration of the FeCl$_3$ solution?

- What is the molar concentration of Cl$^-$ ions?

Exercise 09

We want to prepare a solution S_2 of hydrochloric acid with a concentration of $C_2 = 0.05$ mol/l and a volume of V = 200 ml from a solution S_1 of hydrochloric acid with a concentration of $C_1 = 1$ mol/l. What volume of solution S_1 should be taken?

Exercise 10

Calculate the number of moles of ethanol C$_2$H$_5$O in 1 liter. <u>Given</u> d = 0.79. Also, given the density of air $\rho_{air} = 1$ g/cm^3, and the molar masses of C, H, and O are respectively: 12 g/mol, 1 g/mol, 16 g/mol.

Exercise 11

We have a concentrated hydrochloric acid solution at 37% with a density of 1.18 g/cm³. We take 10 ml of this acid and dilute it in a 1-liter flask. What is the concentration of the resulting solution? Given: $M_{HCl} = 36.5$ g/mol, and the density of air $\rho_{air} = 1$ g/cm³.

Exercise 12

We have a 1 M solution of potassium chloride (KCl) in water. An evaporation reduces the volume to 300 ml.

- What is the number of moles of KCl in the solution before and after water evaporation?

- What is the new concentration of the solution?

- The solubility of KCl is 344 g/l. What will be the final volume of the solution if we evaporate water to the limit of KCl solubility? <u>Given</u>: Molar mass of KCl = 74.55 g/mol.

Exercise 13

Mix 50 ml of a 10^{-2} mol/L $FeCl_3$ solution with 100 ml of a 10^{-1} mol/L NaCl solution. What is the final concentration of Na^+, Fe^{3+}, and Cl^- ions?

Exercise 14

We want to prepare 1 liter of a normal solution of sulfuric acid. We have 98% sulfuric acid with a density of 1.84. How much acid should be taken? Given: Molar mass of $H_2SO_4 = 98$ g/mol, and the density of air $\rho_{air} = 1$ g/cm³.

Exercise 15

An organic compound with the general formula C_xH_yOz is in a gaseous state at a temperature of 23°C and a pressure of 760 mmHg. Its density is d = 1.585, and the percentages of its components are: C = 52.17%, H% = C%/4. Find its general formula.

Exercise 16

An analysis of a 1.23 g sample of an alkane revealed that it contains 0.223 moles of hydrogen (H). What is the empirical formula of the alkane?

Exercise 17

Eosin is a colored chemical species with antiseptic and drying properties. The aqueous solution used has a concentration C = 2.90 $\times 10^{-2}$ mol/l.

- How much eosin needs to be dissolved in distilled water to prepare 250 ml of the solution?

- What is the corresponding mass?

- What is the mass concentration (mass percentage) of eosin in the solution? <u>Given</u>: Molar mass of eosin: M (Eosin) = 693.6 g/mol.

Exercise 18

The alcohol content of a wine is given by the volume value expressed in ml of pure ethanol C_2H_8O present in 100 ml of the wine. A bottle of white wine at 12°has a capacity of 75 cl.

- How much ethanol would need to be added to distilled water to obtain a solution with the same volume and alcohol content as this wine?

- What is the ethanol concentration of this solution?

- Define alcohol poisoning.

<u>Given</u>: Density of pure ethanol: d = 0.79, Density of water: $\rho = 1.0$ g/ml.

Exercise 19

The label of a box of vitamin-enriched aspirin indicates that one tablet contains 500 mg of aspirin (acetylsalicylic acid $C_9H_8O_4$) and 200 mg of vitamin C (ascorbic acid $C_6H_8O_6$).

- Determine the molar masses of aspirin and vitamin C.

- Determine the amounts of aspirin and ascorbic acid in 150 ml of a solution obtained by dissolving one tablet in a glass of water.

- Determine the molar concentrations of aspirin and vitamin C in the above solution.

Exercise 20

Vinegar at 8°C is an aqueous solution primarily containing acetic acid $C_2H_4O_2$. We aim to determine the molar concentration of acetic acid in this vinegar.

- What is the molar mass of acetic acid?

- What is the mass of acetic acid in 1 liter of vinegar, given that the density of acetic acid is $\rho = 1.05\,\text{g/cm}^3$?

- What is the amount of vinegar substance in 1 liter of vinegar? What is the desired concentration?

Exercise 21

At 25°C, the solubility of aspirin $C_9H_8O_4$ is 1.00 g in 300 ml of water: For a higher mass of aspirin, a solution with a volume of 300 ml is considered saturated.

1. What is the maximum molar concentration of an aspirin solution?

2. At 25°C, 400 ml of aspirin solution is prepared from 1.20 g of pure aspirin crystals. Is the solution saturated? What is the molar concentration of the resulting solution? Explain the effect of temperature on dissolution.

Exercise 22

The label of a bottle containing ammonia NH_3 provides the following information: Density: 0.950; mass percentage of ammonia: 28%

1. Determine the molar concentration of this solution.

2. Water density: $\rho = 1.00\,\mathrm{g/cm}^3$

Exercise 23

During a blood analysis, the person's blood sugar level, known as glycemia, is studied. An analysis provides the following results: Fasting glycemia is 8 mmol/l.

1. What does the number 8 correspond to?

2. Convert 8 mmol/l to mol/l.

3. Calculate the molecular molar mass of glucose, which has the chemical formula $C_6H_{12}O_6$.

4. Determine the mass concentration of glucose.

5. Normal glycemia falls within the mass concentration range of 0.75 g/l to 1.10 g/l. Is the person's glycemia normal?

Exercise 24

At a certain temperature, the vapor pressure of pure benzene C_6H_6 is 706.8 mmHg. 15.0 g of a non-volatile, non-electrolyte solute is dissolved in 117 g of benzene at this temperature. The vapor pressure of the solution is then 684 mmHg. Assuming ideal solution behavior, calculate the molar mass of the solute.

Exercise 25

Toluene and benzene form an ideal mixture. At 25°C, their vapor pressures are 28 torr and 95 torr, respectively. What must be the composition of the liquid phase if the molar fraction of benzene is 13 times that of toluene in the vapor phase?

Exercise 26

At 25°C, the vapor in equilibrium with a supposed ideal solution of carbon disulfide CS_2 and acetonitrile CH_3CN has a total pressure of 0.346 atm, with a mole fraction of carbon disulfide equal to 0.855. Calculate the mole fraction of carbon disulfide in the solution, knowing that at this temperature, the vapor pressure of CS_2 is 0.493 atm. Assuming an ideal solution, calculate the molar mass of the solute.

Exercise 27

0.5 g of a compound were dissolved in 50 g of benzene. This solution freezes 0.44°C lower than pure benzene. What is the molar mass of this compound?

Exercise 28

How much urea CON_2H_4 must be added to 40 g of water to obtain a solution that freezes at -8°C?

Exercise 29

Determine the empirical formula of a compound for which 1.627 g produce 3.254 g of CO_2 and 1.331 g of water by combustion, given that it contains only carbon, hydrogen, and oxygen. The measurement of molar mass by cryoscopy results in a 0.86°C depression in the freezing point of the aqueous solution at 4.07 g per 100.0 g of water.

1.3 Exercise Solutions

Exercise 01

1. The atomic number of a chemical element is defined by the number of protons because it never changes, unlike the number of neutrons and electrons.

2.
   - 12 atomic mass units (a.m.u) is the mass of an atom of carbon.
   - 12 g is the mass of one mole of carbon.
   - One mole of electrons contains 6.023×10^{23} electrons.

Exercise 02

In this case, the samples are of different natures. To determine which one contains the most iron, we can consider either the number of moles of iron in each sample, the mass of iron, or the number of iron atoms. Let's opt for the number of moles.

1. 0.2 moles of Fe_2SO_4 contains 0.4 moles of Fe.

2. In the second sample, the number of moles of iron, n, is calculated as $n = \dfrac{\text{mass of iron}}{\text{molar mass of iron}}$. Therefore, $n = \dfrac{20}{56}$, which equals 0.357 moles.

3. In the third sample, the number of moles of iron, n, is calculated as $n = \dfrac{\text{number of atoms}}{\mathscr{N}}$. Therefore, $n = \dfrac{2.5 \times 10^{23}}{6.023 \times 10^{23}}$, which equals 0.415 moles. We can conclude that the third sample contains the most iron.

Exercise 03

1. Number of moles of CuO, $n = \dfrac{\text{mass}}{\text{molar mass}}$. So, $n = \dfrac{1.59}{63.54 + 16} = 0.01999$ moles.

2. Number of moles of Cu = number of moles of O = 0.01999 moles.

3. Number of molecules of CuO = $0.01999 \times 6.023 \times 10^{23} = 0.12 \times 10^{23}$ molecules.

4. Number of atoms of Cu = number of atoms of O = $0.01999 \times 6.023 \times 10^{23} = 0.12 \times 10^{23}$ atoms.

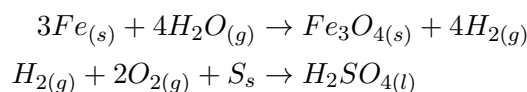**Exercise 04**

Balanced equations:

$$3Fe_{(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + 4H_{2(g)}$$
$$H_{2(g)} + 2O_{2(g)} + S_s \rightarrow H_2SO_{4(l)}$$

Table of Equilibriums:

Equilibrium	Number of Phases	Type of Mixture	Types of Substances
1	2	Heterogeneous	Simple (Fe_s, $H_{2(g)}$), compound ($H_2O_{(g)}$, $Fe_3O_{4(s)}$)
2	3	Heterogeneous	Simple (H_2, O_2, S), compound ($H_2SO_{4(l)}$)

Calculation of gas densities ($H_{2(g)}$, $O_{2(g)}$, $H_2O_{(g)}$): Let the density (volumic mass) of air be $\rho_{\text{air}} = \dfrac{m}{V} = 1.293 \times 10^{-3}$ g/cm^3, and $\rho'_{\text{gas}} = \dfrac{m'}{V}$ be the density of a gas. The density of a perfect gas compared to air is given by $d = \dfrac{\rho'}{\rho} = \dfrac{m'/V}{m/V} = \dfrac{m'}{m}$ for the same volume V (1 cm^3). We calculate the mass of each gas for 1 cm^3. Note that 1 molecule of a perfect gas occupies a volume of 22.4 liter, so 1 cm^3 of that gas corresponds to the mass in grams equivalent to:

$$1 \text{ mole} \rightarrow M(\text{g/mole}) \rightarrow 22.4 \text{ L} = 22400 \text{ cm}^3$$
$$m'(\text{g}) \rightarrow V = 1 \text{ cm}^3$$

Therefore, $m = M \times \dfrac{1 \text{ cm}^3}{22400 \text{ cm}^3}$

$$\text{For } H_2 : M = 2 \text{ g/mole} \Rightarrow m' = \frac{2}{22400} = 8.93 \times 10^{-5} \text{ g}$$

$$\text{For } O_2 : M = 32 \text{ g/mole} \Rightarrow m' = \frac{32}{22400} = 1.43 \times 10^{-3} \text{ g}$$

$$\text{For } H_2O : M = 18 \text{ g/mole} \Rightarrow m' = \frac{18}{22400} = 8.04 \times 10^{-4} \text{ g}$$

The density of a perfect gas compared to air is:

$$\text{For } H_2 : d_{H_2} = \frac{8.93 \times 10^{-5} \text{ g/cm}^3}{1.293 \times 10^{-3} \text{ g/cm}^3} = 6.90 \times 10^{-2}$$

$$\text{For } O_2 : d_{O_2} = \frac{1.43 \times 10^{-3} \text{ g/cm}^3}{1.293 \times 10^{-3} \text{ g/cm}^3} = 1.10$$

$$\text{For } H_2O : d_{H_2O} = \frac{8.04 \times 10^{-4} \text{ g/cm}^3}{1.293 \times 10^{-3} \text{ g/cm}^3} = 0.621$$

Note: The formula $d = M/29$ can also be applied.

Exercise 05

1) Molarity (M, mol/l) is also known as molar concentration (C) and can be calculated as $C = \dfrac{n}{V} = \dfrac{(\dfrac{n}{M})}{V}$.

The molar mass of HCl is $35.5 + 1 = 36.5$ g/mol.
$n_{HCl} = \dfrac{m}{M} = \dfrac{8.36}{36.5} = 0.229$ moles.
$$C = \dfrac{0.229}{20 \times 10^{-3}} = 11.45 \text{ mol/liter.}$$

2) Normality (N) is calculated as $N = C \times Z$, where for HCl, $Z = 1$, representing the number of H^+ ions that can be released. So, $N = (11.45\,\text{mol/l}) \times 1 = 11.45$.

3) Molality (b) is defined as $\dfrac{\text{moles of solute}}{\text{mass of solvent}}$ (in mol/kg).
We have $\rho = \dfrac{m_{\text{solution}}}{V_{\text{solution}}}$.
$m_{\text{solution}} = (\rho \times V) = (1.18\,\text{g/cm}^3) \times (20\,\text{cm}^3) = 23.6$ g.

Exercise 06

1) The number of moles contained in 10 g of NaCl is given by $\dfrac{mass}{molar\ mass}$, which is equal to 0.17094 moles.

2) The molar concentration (C) is calculated as $\dfrac{number\ of\ moles}{volume}$. Therefore, C $= \dfrac{0.17094}{205 \times 10^{-3}} = 0.68376$ mol/l.

Exercise 07

1) To determine the mass to be weighed, we first need to find the number of moles contained in 250 ml.
We have a molar concentration of 2.5 mol/l.
$\Rightarrow$ n = Molar concentration $\times$ volume
$\Rightarrow$ n $= 2.5 \times 250 \times 10^{-3} = 0.625$ moles.
$\Rightarrow$ The mass (m) that needs to be weighed is equal to: number of moles (0.625) $\times$ the molar mass of $CuSO_4$.
$\Rightarrow$ m $= 0.625 \times (63.55 + 32 + 16) = 69.7187$ g.

2) To determine the concentration of the resulting solution, we need to know the number of moles in 10 ml of the stock solution.
The concentration of the stock solution is 2.5 mol/l. $\Rightarrow$ In 1000 ml, there are 2.5 moles. $\Rightarrow$ 10 ml contains $\dfrac{10 \times 2.5}{10^{-3}} = 0.025$ moles.
The concentration of the new solution (C) is equal to $\dfrac{0.025}{250 \times 10^{-3}} = 0.1$ mol/l.

Exercise 08

1) The molar mass of $FeCl_3 = (55.9 + 3 \times (35.5)) = 162.4$ g/mol.

2) Molar concentration (C) $= \dfrac{\text{number of moles}}{\text{volume}}$.

$\Rightarrow$ C $= \dfrac{(\dfrac{5}{162.4})}{250 \times 10^{-3}} = 0.12315$ mol/l.

3) Molar concentration of $Cl^- = 3 \times 0.12315 = 0.369458$ mol/l.

Exercise 09

To determine the volume to be withdrawn, we apply the following relationship: $C_1 \times V_1 = C_2 \times V_2$. Knowing that (C_2, V_2) are the data for solution 2 and (C_1, V_1) are the data for solution 1.

$\Rightarrow$ The volume V_1 to be withdrawn $= \dfrac{C_2 \times V_2}{C_1}$.

$\Rightarrow V_1 = \dfrac{0.05 \times 200 \times 10^{-3}}{1} = 0.01$ l $= 10$ ml.

Exercise 10

To find the number of moles, we must first find the mass of ethanol.

We have the density $d = \dfrac{\rho_{d\text{ ethanol}}}{\rho_{\text{air}}}$.

$\Rightarrow \rho_{d\text{ ethanol}} = 0.79$ g/cm^3, while knowing that $\rho = \dfrac{\text{mass}}{\text{volume}}$.

The volume is 1 liter

$\Rightarrow$ Mass (m) $= 0.79$ g.

$\Rightarrow$ The number of moles n $= \dfrac{\text{mass}}{\text{molar mass}}$.

$\Rightarrow$ n $= \dfrac{0.79}{(2 \times 12) + (1 \times 5) + (16)} = 0.01755$ mole.

Exercise 11

We are looking for the mass of the solution, knowing that the density $d = \dfrac{\rho_{\text{HCl}}}{\rho_{\text{air}}}$. $\Rightarrow \rho_{\text{HCl}} = 1.18$ g/cm^3.

$\rho_{\text{HCl}} = \dfrac{\text{mass}}{\text{volume}}$ and with a volume of 1000 ml.

$\Rightarrow$ mass (m) $= 1000 \times 1.18 = 1180$ g.

A concentrated HCl solution at 37% means that in 1000 g of the solution, there is 37% pure HCl.

$\Rightarrow$ 1180 g of the solution contains: $\dfrac{37 \times 1180}{100} = 436.6$ g of pure HCl.

$\Rightarrow$ 1000 ml of the solution contains 436.6 g of HCl.

$\Rightarrow$ The withdrawn volume (10 ml of the solution) corresponds to $\dfrac{10 \times 436.6}{1000} = 4.366$ g of HCl.

So the number of moles contained in 10 ml of the solution $= \dfrac{4.366}{36.5} = 0.1196$ mole.

$\Rightarrow$ The concentration C = $\dfrac{\text{number of moles}}{\text{volume}}$ = $\dfrac{0.1196}{1 liter}$ = 0.1196 mol/l.

Exercise 12

1) We have 1 liter of KCl with a concentration (C) of 1M and the molar mass of KCl = 74.55 g/mol $\Rightarrow$ the number of moles (n) = C $\times$ V = 1 mole. Before and after evaporation, the number of moles is the same and equal to 1 mole.

2) The new concentration of the solution C' = $\dfrac{1}{300 \times 10^{-3}}$ = 3.333 mol/l.

3) To find out the solubility volume, we must find the mass of KCl in the solution.

We have the molar mass of KCl = 74.55 g/mol

$\Rightarrow$ the mass (m) = 1 $\times$ 74.55 = 74.55 g. Knowing that the solubility limit is 344 g/l $\Rightarrow$ the final volume of the solution will be equal to $\dfrac{74 \times 1000}{344}$ = 216.715 ml.

Exercise 13

1) We need to calculate the number of moles of $FeCl_3$ in 50 ml of the solution and consequently the number of moles of Fe and Cl^-. The number of moles (n) of $FeCl_3$ = (0.01 mol/l) $\times$ (50 $\times 10^{-3}$ l) = 0.0005 = 5 $\times 10^{-4}$ moles.

$\Rightarrow$ In the $FeCl_3$ solution, we have the number of moles of Fe^+ = 5 $\times 10^{-4}$ mol, and the number of moles of Cl^- = 3 $\times$ 5 $\times 10^{-4}$ = 15 $\times 10^{-4}$ mol/l.

In the NaCl solution, the number of moles of NaCl = (0.1) $\times$ 100 $\times 10^{-3}$ l = 0.01 moles.

$\Rightarrow$ Number of moles of Na^+ = Number of moles of Cl^- = 0.01 moles.

$\Rightarrow [Fe^+] = \dfrac{5 \times 10^{-4}}{(50 + 100) \times 10^{-3}}$ = 3.33 $\times 10^{-3}$ mol/l.

$\Rightarrow [Cl^-] = \dfrac{(15 \times 10^{-4}) + (0.01)}{(50 + 100) \times 10^{-3}}$ = 7.66 $\times 10^{-2}$ mol/l.

$\Rightarrow [Na^+] = \dfrac{0.01}{(50 + 100) \times 10^{-3}}$ = 6.66 $\times 10^{-2}$ mol/l.

Exercise 14

In this case, we want to prepare a 1N sulfuric acid solution. To do this, we need to find the molar concentration of the solution to be prepared, and consequently, find the number of moles (or the mass) of pure H_2SO_4 to be taken from the stock solution.

We know that normality (N) = C $\times$ Z (Z is the number of exchanged protons) with $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$.

$\Rightarrow$ Z = 2 $\Rightarrow$ C = 1/2 = 0.5 mol/l.

Knowing that the density of air ρ_{air} = 1 g/cm^3 $\rightarrow \rho_{sulfuric\,acid}$ = 1.84 g/cm^3

$\Rightarrow$ the mass of H_2SO_4 = 0.5 $\times$ 98 = 49 g/liter.

And knowing that $\rho_{acid} = \dfrac{mass}{volume}$

$$\Rightarrow \text{Volume to be taken} = \frac{49}{1.84} = 26.630 \text{ cm}^3.$$

Exercise 15

In this case, we calculate the mass of carbon. We have the number of moles of hydrogen equal to 0.223 moles, so the mass of hydrogen is 0.223 g. The mass of carbon is (the mass of the alkane - the mass of hydrogen) = (1.23 - 0.223) = 1.007 g. Regarding the number of atoms, we have the following ratio: $\dfrac{(1.007/12)}{0.223} = \dfrac{n}{2n+2} \Rightarrow n \approx 3$.

The empirical formula of the alkane is C_3H_8.

Exercise 16

We have an organic compound $C_xH_yO_z$ with a density of 1.585. The conditions of 23°C and 760 mmHg allow us to apply the following gas law: $d = \dfrac{M}{29} \Rightarrow M = 46$ g/mol. We have C% = 52.17% and H% = C%/4, so O% = 100% - (52.17% + (52.17/4) = 34.79%. To find x, y, and z, we apply:

$$x \approx \frac{46 \times 52.17}{12} \approx 2$$
$$y \approx \frac{46 \times 13.03}{1} \approx 6$$
$$z \approx \frac{46 \times 34.79}{12} \approx 1$$

So, the compound is C_2H_6O.

Exercise 17

1) Calculation of the corresponding mass:

We have $C = \dfrac{number\ of\ moles}{volume} \Rightarrow C = \dfrac{\frac{Masse}{masse\ molaire}}{volume}$.

Therefore, mass (m) = C × Volume × molar mass = $2.9 \times 10^{-2} \times 250 \times 10^{-3} \times 693.6 = 5.0286$ g.

2) The mass concentration = $\dfrac{mass}{volume} = \dfrac{5.0286}{250 \times 10^{-3}} = 20.1144$ g/l.

Exercise 18

1) Amount of ethanol required. First step: Volume of pure ethanol V(ol) present in 75 cl of this wine. We note V (b) the volume of the bottle: V (b) = 75 cl = 750 ml. We note V the volume of pure ethanol present in V_0 = 100 ml of this wine.

Wine	$V_0 = 100$ ml	$V(b) = 75$ cl = 750 ml
Ethanol	V = 12 ml	V(ol)

We use the following relation:

$V(ol) = V \times \dfrac{V(b)}{V_0} = 12 \times 750/100 = 90$ ml.

2) Concentration of the solution: We have d = 0.79 and $\rho_{water} = 1$ g/cm^3.

Since d = $\dfrac{mass\ of\ the\ volume}{mass\ of\ the\ same\ volume\ of\ water}$, we get $0.79 = \dfrac{mass}{90}$ (because the mass of 90 ml of water is equal to 90 g).

Therefore, mass $= 0.79 \times 90 = 71.1$ g. The number of moles $= \dfrac{71.1}{(12 \times 2) + (8) + (16)} =$ 1.48125 moles.

So, the concentration C $= \dfrac{1.48125}{750 \times 10^{-3}} = 1.975$ mol/l.

Exercise 19
Hints:

1) Amount of substance of aspirin: $n_{asp} \simeq 2.78 \times 10^{-3}$ moles.

2) Amount of substance of ascorbic acid: $n_{asb} \simeq 1.14 \times 10^{-3}$ moles.

Molar concentrations:

$C_{asp} \simeq 1.85 \times 10^{-2}$ mol/l

$C_{asb} \simeq 7.58 \times 10^{-1}$ mol/l

Exercise 20
Hints:

1) Amount of substance of vinegar in one liter: $n \simeq 1.4$ moles

2) Concentration of acetic acid: $C \simeq 1.4$ mol/l

Exercise 21
Hints:

1) Maximum concentration: $C \simeq 1.85 \times 10^{-2}$ mol/l.

2) Concentration of the obtained solution: At 25 °C, the solubility of aspirin is 1.0 g in 300 ml, so for 400 ml of solution, we can dissolve: $m_{max} = 1.0 \times (400/300)$.

Therefore, $m_{max} \simeq 1.33$ g.

Since $m < m_{max}$, the solution is not saturated.

Concentration of the obtained solution: $C \simeq 1.67 \times 10^{-2}$ mol/l.

Exercise 22
Hints:

Molar concentration of this solution.

- Mass percentage: 28.0%. This means that 100 g of solution contains 28.0 g of pure ammonia.

- Molar mass of ammonia: M = 17 g/mol.

- Mass of 1.00 liter of commercial solution: $m \simeq 950$ g.

- Mass of ammonia in 1.00 liter of commercial solution: $m(NH_3) \simeq 266$ g.

- Mass of ammonia in 1.00 liter of the commercial solution: $m(NH_3) \approx 266$ g.

- Amount of ammonia substance: $n(NH_3) \approx 15.7$ mol.

- Concentration of the commercial solution: $C \approx 15.7 \times 10^{-2}$ mol/l.

Exercise 23

1) Molar concentration of glucose in millimoles per liter.
2) 0.008 mol/l.
3) Molar mass (M) of $C_6H_{12}O_6 = 180$ g/mol.
4) $C_m = 1.44$ g,
5) NO, $1.44 > 1.10$.

Exercise 24

$$X_{C_6H_6} = \frac{684}{706.8}$$

$$X_s = 1 \text{-} \frac{684}{706.8} = \frac{22.8}{706.8}$$

$$n_{C_6H_6} = \frac{117}{78} = 1.5 \text{ mol}$$

$$\frac{22.8}{706.8} = \frac{n_s}{n_s + 1.5}$$

$$n_s = 0.050 \text{ mol}$$

$$M_s = \frac{m_s}{n_s} = \frac{15}{0.05} = 300 \text{ g/mol.}$$

Exercise 25

Let X_t and X_b be the sought mole fractions:

$$\begin{cases} P_t = 3P_b & (1) \\ P_t = X_t \times 28 & (2) \\ P_b = X_b \times 95 & (3) \\ X_t + X_b = 1 & (4) \end{cases}$$

Solving this system of 4 equations with 4 unknowns yields: $X_t = 0.91006$, $X_b = 0.0894$

Exercise 26

In the vapor phase:

$$0.855 = \frac{P_{CS_2}}{0.346}$$

$$P_{CS_2} = 0.296 \text{ atm}$$

In the liquid phase (Raoult's law):

$$0.296 = X_{CS_2} \times 0.493$$

$$X_{CS_2} = 0.600$$

Exercise 27

Let b = benzene and s = solute

$$\mu_s = \frac{1000 \times n}{m_b} = \frac{1000 \times m_s}{M_s \times m_b}$$

$\Delta T = fus\mu_s$, so $M_s = \dfrac{K_{fus} \times 1000 \times m_s}{m_b \times \Delta T} = \dfrac{1000 \times 4.90 \times 0.5}{0.44 \times 50}$

$\Rightarrow$ $\boxed{M_s = 111g/mol}$

Exercise 28

Let μ = urea and e = water

$\mu_\mu = \dfrac{1000 \times n}{m_e} = \dfrac{1000 \times m_\mu}{M_\mu \times m_e}$

$\Rightarrow 8 = 1.86 \times \dfrac{1000 \times m_\mu}{60 \times 40}$, so $m_\mu = 10.3g$

Exercise 29

Let c = compound and e = water

$$\mu_c = \frac{1000 \times n_c}{m_e} = \frac{1000 \times m_c}{M_e \times m_e}$$

$\Delta = K_{fus}\mu_c$, so:

$$M_c = \frac{K_{fus} \times 1000 \times m_c}{m_e \Delta T} = \frac{1000 \times 1.86 \times 4.07}{0.86 \times 100} \simeq 88.0 \text{ g/mol.}$$

The mass of carbon in 1 mole = 88 g.

$$\text{m} = \frac{3.254 \times 12}{44} \times \frac{88.0}{1.627} \simeq 48.0 \text{ g} = 4 \text{ mol.}$$

Hydrogen in 1 mole = 88 g.

88-48-8 =32 , 32g = 2 mol $\rightarrow$ empirical formula: $C_4H_8O_2$

1.4   Problems

Problem 01

What volume of 0.250 M Na_2CO_4 will be needed in order to obtain 8.10 g of Na_2CO_4 ?

Solution

If V = liters of solution needed it must supply the number of moles contained in 8.10 g of Na_2CO_4

$$\text{Moles of } Na_2CO_4 \text{ needed} = \frac{8.10 \text{ g } Na_2CO_4}{162.0 \frac{g\ Na_2CO_4}{mole\ Na_2CO_4}} = 0.0500 \text{ moles}$$

$$\text{Moles of } Na_2CO_4 \text{ in } V \text{ liters} = (0.250\frac{moles\ Na_2CO_4}{liter})$$

$$= 0.250V \text{ moles}$$

$$V = 0.200 \text{ liter} = 200 \text{ ml needed}$$

This problem illustrates the two most common ways of calculating moles of a compound: (a) weight divided by mole weight, and (b) molarity times volume in liters.

Problem 02

Prepare a 2.00 m (molality)naphthalene ($C_{10}H_8$) solution using 50.0 g CCl_4 as the solvent.

Solution

You are given the molality of the solution and the weight of the solvent, from which you can find x , the number of moles of $C_{10}H_8$ needed.

$$\text{Molality} = \text{m} = \frac{x\ moles\ C_{10}H_8}{0.0500 Kg\ CCl_4} = 2.00$$

$$\text{x} = 0.100 \text{ moles } C_{10}H_8 \text{ needed}$$

$$\text{Weight of } C_{10}H_8 \text{ needed} = (0.1000 \text{ moles } C_{10}H_8)(128\ \frac{g\ C_{10}H_8}{moles\ C_{10}H_8})$$

$$= 12.8 \text{ g } C_{10}H_8$$

To prepare the solution, dissolve 12.8 g $C_{10}H_8$ in 50.0 g CCl_4. If you knew that the density of CCl_4 is 1.59 g/ml, you could measure out :

$$\frac{50}{1.59} = 31.4 \text{ ml } CCl_4$$

Problem 03

Prepare a 0.0348 mole fraction solution of sucrose ($C_{12}H_{22}O11$, mole weight = 342 g/mole), using 100 g (that is, 100 ml)of water.

Solution

You are given the mole fraction of sucrose and the moles of water

$$\frac{100}{18} = 5.55 \text{ moles}$$

What you don't know is x the moles of sucrose needed By definition,

$$\text{mole fraction} = 0.348 = \frac{x \, moles \, sucrose}{(5.55 \, moles \, H_2O) + (x \, mole \, sucrose)}$$

Therefore,

$$x = \frac{(5.55)(0.0348)}{1 - 0.0348} = 0.200 \text{ mole sucrose.}$$

$$\text{Weight of sucrose needed} = (0.200 \text{ mole sucrose}) \times (342 \, \tfrac{g \, sucrose}{mole \, sucrose})$$
$$= 68.4 \text{ g sucrose.}$$

Prepare the solution by dissolving 68.4 g sucrose in 100 g water.

Problem 04

Commercial concentrated sulfuric acid is labeled as having a density of 1.84 g/ml and being 96 0% H_2SO_4 by weight Calculate the molarity of this solution.

Solution

This is a typical conversion problem in which we want to go from grams of solution per liter to moles of H_2SO_4 per liter

$$(1840\frac{g \, solution}{liter})(0.960\frac{g \, H_2SO_4}{g \, solution})(\frac{1 \, mole \, H_2SO_4}{98.1 \, g \, H_2SO_4}) = 18.00 \, \frac{mole \, H_2SO_4}{liter}$$
$$= 18 \text{ M}$$

Problem 05

What are (a) the molality and (b) the mole fraction of the commercial H_2SO_4 solution in the previous problem ?

Solution

- (a)To find the molality we need to know, for a given amount of solution, the moles of H_2SO_4 and the kg of H_2O. If we take a liter of solution, we shall have 1840 g solution, of which 4.0% is water, so $(0.040)(1840$ g$) = 74$ g H_2O.Because there are 18.0 moles of H_2SO_4 in this liter, we have :

$$\text{molality} = \text{m} = \frac{18.0 \, moles \, H_2SO_4}{0.074 \, kg \, H_2O} = 243 \text{ molal } H_2SO_4$$

- (b)To find the mole fraction, we need to know (for a given amount of solution) the moles of H_2SO_4 and the moles of H_2O. If we take a liter of solution, we shall have 18.0 moles of H_2SO_4 and

$$\frac{74 \, g \, H_2O}{18 \, \frac{g \, H_2O}{mole \, H_2O}} = 4.1 \text{ moles of } H_2O$$

Therefore the mole fraction is :

$$\chi_{H_2SO_4} = \frac{18.0 \, moles \, H_2SO_4}{(18.0 \, moles \, H_2SO_4) + (4.1 \, moles \, H_2O)} = 0.814$$

Note that it is not possible to convert from molarity to molality or mole fraction unless some information about the density or weight composition of the solution is given.

Problem 06

What volume of 18.0 M H_2SO_4 is needed for the preparation of 2.00 liters of 3.00 M H_2SO_4 ?

Solution

We are given the initial and final concentrations of the two solutions, along with the final volume Therefore,

$$(18.0 \, \tfrac{moles}{liter} \, (\text{V liters}) = (2.00 \text{ liters}) \, (3.00 \, \tfrac{moles}{liter})$$
$$\text{V} = \frac{(2.00)(3.00)}{(18.0)} = 0.333 \text{ liter}$$

To prepare the solution measure out 333 ml of 18.0 M H_2SO_4 and dilute it to 2.00 liters in a volumetric flask Shake well for uniformity because the interaction of concentrated H_2SO_4 with H_2O evolves mm h heat and can cause hazardous splattering, it is better to do a partial dilution with about one liter of water first in a beaker Then, after cooling, transfer the contents to the volumetric flask, and complete the dilution The final dilution to the mark must be made with the solution at room temperature.

Chapter 2

Major Constituents of Matter

2.1 Important Concepts and Course Review

♣ **The electron** is an **elementary** particle, point-like (size smaller than 10^{-18} m), negatively charged, moving around the atomic nucleus. The distance between the center of the atom and the electrons is approximately 10^4 to 10^5 times greater than the radius of the nucleus.

The atomic nucleus is composed of two types of **nucleons** (= stable particles, constituents of the nucleus), the **protons** and the **neutrons**.

♠ A nuclide is denoted as $^A_Z\mathbf{X}$.

X: Symbol of the atom, uppercase letter or uppercase letter followed by a lowercase letter.

A: Mass number (represents the total number of nucleons).

Z: Charge number (represents the total number of protons). (A - Z) thus gives the number of neutrons.

Z also gives the number of electrons present in the atom (not in ions).

♣ Key characteristics of the electron, proton, and neutron.

Particle and Symbol	First Measurements by Authors	Charge	Mass
Electron e^-	J. J. Thomson (1897), R. A. Millikan (1911)	$-e = -1.602 \times 10^{-19}$ C	9.1094×10^{-31} kg
Protons p	E. Rutherford (1910)	$+e = +1.602 \times 10^{-19}$ C	1.6726×10^{-27} kg
Neutron n	J. Chadwick (1932)	0	1.6749×10^{-27} kg

♣ The isotopic abundance of a particular isotope in a natural sample of atoms belonging to a given element is represented by the molar fraction or molar percentage of that isotope in the sample.

• The relative atomic mass of an isotope is the ratio of the mass of an atom of that isotope to one-twelfth of the mass of a carbon-12 atom, $_{6}^{12}$C.

$$\text{Ar}(_{Z}^{A}\text{X}) = \frac{m_{\text{an atom }(_{Z}^{A}X)}}{\dfrac{1}{12}m_{\text{an atom }(_{6}^{12}C)}} \text{ (dimensionless)}.$$

(Ar: relative atomic mass is generally close to mass number A)

• The relative atomic mass of an element is the ratio of the average mass of an atom for the natural isotopic composition to one-twelfth of the mass of a $_{6}^{12}$C atom. $\text{Ar}(_{Z}\text{X}) = \sum_{i} \dfrac{y_i}{100} Ar_i$ (dimensionless).

Where y_i is the isotopic abundance (in number of atoms) of isotope i with relative isotopic mass Ar_i.

2.2 Exercise Statements

Exercise 01

Joseph John Thomson devised a device in which a beam of electrons is deflected as it passes between two plates where an electric field prevails. The following study concerns the motion of an electron from the beam that enters between two parallel and horizontal plates P_1 and P_2, in a region where a uniform electric field is assumed to be perpendicular to the two plates. At time $t = 0$ s, the electron arrives at point O (origin of the Oxy coordinate system) with a velocity v_0 such that the vector forms an angle α with the Ox axis.

Given:

Figure 2.1: Experimental Setup
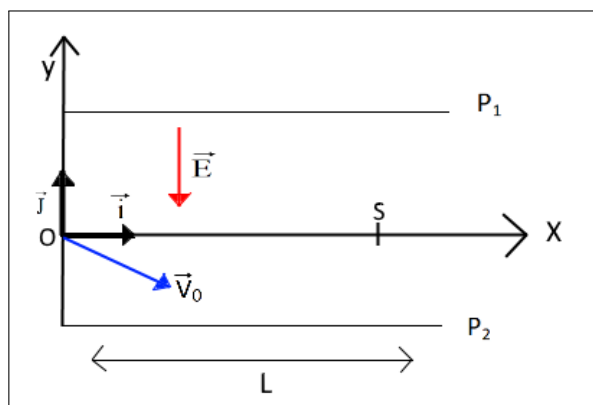
- Particle: electron
- $\alpha = 15°$
- $v_0 = 8.20 \times 10^5$ m/s
- E = 670 V/m
- $L = 9.0 \times 10^{-2}$ m
- $m_e = 9.11 \times 10^{-31}$ kg
- $e = 1.60 \times 10^{-19}$
- g = 9.81 m/s^2

1. Determine the polarity of plates P_1 and P_2. Justify your answer.

2. Provide the vector expression for the electric force experienced by the electron.
   Compare the direction and magnitude of the electric force F_e to that of the electric field E.
   Represent the electric force on the diagram.

3. Show that the weight of the electron is negligible compared to the electric force.

Exercise 02

In J.J. Thomson's experiment, the deflection of an electron beam by the electric field E $= 3.6 \times 10^{-4}$ V/m is canceled out by the opposing action of a magnetic field with induction B $= 9 \times 10^{-4}$ Tesla acting in the same space as E.

1) Determine the velocity of the electrons and their kinetic energy.
2) What is the accelerating potential V that must be applied between the cathode and the anode to give the electrons this kinetic energy? Given: $m_e = 9.1 \times 10^{-31}$ kg; $|e^-| = 1.6 \times 10^{-19}$ C.

Exercise 03
In Millikan's experiment, the motion of an oil drop introduced between the horizontal plates of a planar capacitor is studied using a microscope. A adjustable potential difference $V_A - V_B = U_0$ is applied between the plates, creating a uniform electric field E. The distance between the plates is d. In the presence of the electric field, the drop attains a constant velocity V_2 greater than V_1, with its motion remaining vertical and descending. We measure the value of V_2. The known constants during the experiment are: g, η, ρ (ρ is the density of the oil); the settings U_0 and d; and the measurements V_1 and V_2. We neglect the Archimedes' buoyancy force relative to the weight of the drop.

1- Using dimensional analysis, express the SI unit of viscosity η.
2- Derive the expression for the radius in terms of velocity V_1 and relevant data.
3- Establish the expression for the electronic charge in terms of r, V_1, and V_2.
4- A series of measurements on several drops yield the following results: 3.1×10^{-19} C; 6.4×10^{-19} C; 1.6×10^{-19} C; 9.6×10^{-19} C; and 11.2×10^{-19} C. Interpret these results.

Exercise 04
A droplet of oil with radius r and mass m is subjected to Millikan's experiment. When the droplet carries a charge q, it remains stationary between the plates of the capacitor. If the charge is equal to $2q$, the droplet rises with a velocity V. Calculate this velocity. Given: r = 1.41×10^{-6} m; m = 105.5×10^{-16} g; $\eta = 1.8 \times 10^{-5}$; g = 9.81. Units are in the SI system. Neglect Archimedes' buoyancy (air's buoyancy on the droplet).

Exercise 05
In a MILIKAN-type device, we study the behavior of a single charged droplet.

a. In the absence of an electric field, the droplet descends by 2.61 cm in 12 seconds. Determine the radius and mass of the droplet.

b. An electric field is applied to the droplet, and it becomes stationary. The capacitor plates are 2 cm apart, and the potential difference is 4320 volts.

   1. What is the charge of the droplet?

2. Compare this charge to the elementary charge of the electron and draw a conclusion.

Given: $\rho = 900$ kg/m^3; $\eta = 18 \times 10^{-6}$ MKSA; g $= 9.81$ m/s^2.

Exercise 06
The MILIKAN experiment is used to track the free fall of an oil droplet in the air, and its velocity is equal to 0.217 mm/s.

a. Under the influence of an electric field $\vec{E}$, the droplet acquires a charge of value 6.49×10^{-19} Cb and rises with a velocity of 2.174×10^{-4} mm/s. Calculate the value of E.

b. During the experiment, the droplet acquires an elementary charge. Calculate the new velocity under the influence of the same electric field $\vec{E}$.

Exercise 07
We analyze a mixture of two isotopes of Boron B using the Bainbridge spectrometer. Two ions with charge $+1$ are subjected to the action of both electric and magnetic fields, such that E/B $= 4.5 \times 10^5$ m/s^{-1}. An ion $^{12}C^+$ heavier than the Boron ions is introduced. In the presence of a magnetic field B $= 0.2$ T, the three ions separate, and the deviation radius of the $^{12}C^+$ ion is 24.92 cm on the photographic plate where two points are observed at distances of 4.17 cm and 8.34 cm from the $^{12}C^+$ ion.
1- Calculate the atomic mass of the two Boron ions.
2- The heaviest isotope of Boron is 4.3 times more abundant than the lighter isotope. Calculate the natural atomic mass of Boron.

Exercise 08
a) Convert the masses of the proton and neutron into unified atomic mass units (u).
b) Deduce the sum of the masses of the nucleons in helium $^4_2$He, expressed in u.
c) Given that the mass of an α particle is 4.0015 u, calculate the binding energy of the helium nucleus in MeV/nucleon.

Exercise 09
Natural chlorine, with a mass of 35.5 atomic mass units (a.m.u), is a mixture of two isotopes, ^{35}Cl and ^{37}Cl.
a) What are their respective proportions? What is the average molecular mass of dichlorine Cl_2?
b) However, just as there are no atoms with a mass of 35.5, there are no molecules of Cl_2 with a mass of 71 either.
Dichlorine is a mixture of molecules having various possible isotopic compositions. How many different types of Cl_2 molecules exist?

c) There are three types of Cl_2 molecules, knowing that the two combinations Cl**Cl** and **Cl**Cl are equivalent (with Cl representing isotope 35 and **Cl** representing isotope 37). What are their relative proportions?

d) Calculate the molecular mass of dichlorine based on the weighted average of the molecular masses (70, 72, and 74) of the different types of molecules. What observation can you make? e) Same questions for $AlCl_3$ as in the previous parts (b, c, and d) for Cl_2, with the atomic mass of Al being 27.

2.3   Exercise Solutions

Exercise 01

1. Plate P_1 is positively charged, and plate P_2 is negatively charged because the electric field lowers potentials, and it is directed from plate P_1 to plate P_2.

$F_e = q \times E = -e \times E$
We can deduce that the vectors for
2. electric force and electric field have the same direction but are in opposite sens.
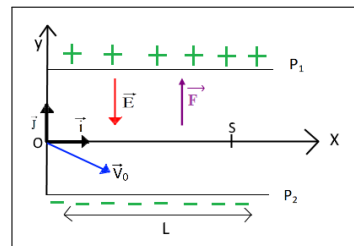
Figure 2.2: Experimental Setup

3. $F_e = e \times E = 1.60 \times 10^{-19} \times 670 = 1.70 \times 10^{-16}$ N
$P = m_e \times g = 9.11 \times 10^{-31} \times 9.81 = 8.94 \times 10^{-30}$ N
$\dfrac{F_e}{P} = \dfrac{1.70 \times 10^{-16}}{8.94 \times 10^{-30}} = 1.20 \times 10^{13}$
Therefore, the weight of the electron is negligible compared to the electric force.

Exercise 02
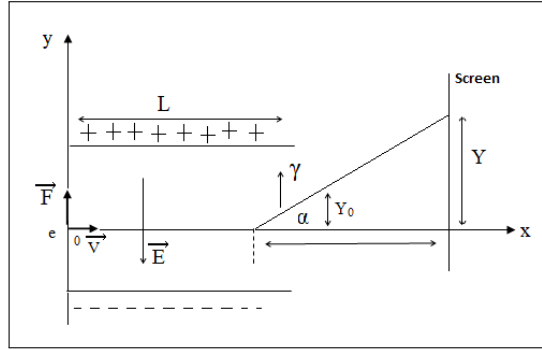
Figure 2.3: Experimental Setup

When $\bar{e}$ (antielectrons) are deflected due to an electric field E over a distance L, they are subject to the force $F = -q \times E$, and an electric charge q moving in a magnetic induction field B with a velocity V is subjected to the magnetic force:

$F_{\text{magnetic}} = q \times (V \wedge B)$.

According to Laplace's law, its model is: $F_{\text{magnetic}} = q \wedge B \sin \alpha$; $\alpha = 90°$

$\Rightarrow F_{\text{magnetic}} = q \wedge B$

To measure V, we must compensate for the deflection caused by the electric field with an opposing magnetic field B, that is: $q \times E = q \times V \times B$

$\rightarrow V = \dfrac{E}{B} = 4 \times 10^7 \, \text{m/s}$,

Similarly, $E_{\text{kinetic}} = q \times V = (1/2) \times m \times V^2$

So, $E_{\text{kinetic}} = 7.28 \times 10^{-16} \, \text{J}$

Now, $E_{\text{kinetic}} = q \times V = (1/2) \times m \times V^2$;

$$\Rightarrow V = \frac{E_{\text{kinetic}}}{q} = 4550 \, \text{V}$$

Exercise 03

1) η; the viscosity constant, $F_{Stokes} = 6\pi\eta r v$

$F : \text{kg} \times \text{m} \times \text{s}^{-2} \rightarrow \eta = \dfrac{F}{6\pi r v} = \dfrac{\text{kg} \times \text{m}^{-1} \times \text{s}^{-1}}{\text{m} \times \text{m} \times \text{s}^{-1}}$

$$\boxed{\eta = \text{kg} \times \text{m}^{-1} \times \text{s}^{-1}}$$
$$\Downarrow$$
$$\boxed{\eta = M \times L^{-1} \times T^{-1}}$$

2) Expression of the radius as a function of V_1 in the absence of E (Figure 2.4)
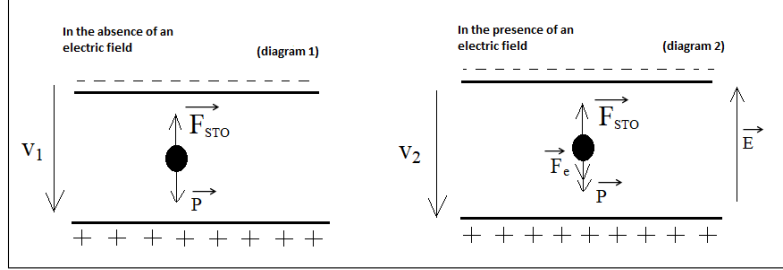
Figure 2.4: Millikan's Oil Drop Experiment 1911

At equilibrium, the sum of forces acting on the droplet is zero: $\sum \vec{F} = \vec{0}$
Force balance on the droplet: $\vec{P} + \vec{F}_{Stokes} = \vec{0}$
By projecting into a vertically downward-oriented axis,
we obtain: $P - F_{Stokes} = 0$, and we get $P = F_{Stokes}$, where $(\frac{4}{3}\pi r^3 \rho_h)$ is the
mass of the droplet and $F_{Stokes} = 6\pi\eta r v_1$

$$P = m \times g \Rightarrow m \times g = 6\pi\eta r v_1$$
$$\Rightarrow \frac{4}{3}\pi r^3 \rho_h \times g = 6\pi\eta r v_1$$
$$\Rightarrow r = \sqrt{\frac{g \times \eta v_1}{2 \times \rho_h}}$$

3) Establishment of the expression for the electronic charge q
At equilibrium, the sum of forces acting on the droplet is zero: $\sum \vec{F}_i = \vec{0}$
Force balance on the droplet: $\vec{P} + \vec{F}_{Stokes} + \vec{F}_e = \vec{0}$, where the electric force
is given by: $\vec{F}_e = q \times \vec{E}$ and $F_{Stokes} = 6\pi\eta r v_2$
We assume $q > 0$ and a field oriented from top to bottom.
By projecting onto a vertically downward-oriented axis, we obtain: $P + F_e = F_{Stokes}$
$\Rightarrow m \times g + q \times E = 6\pi\eta r v_2$ with $m \times g = 6\pi\eta r v_1$

$$6\pi\eta r v_1 + q \times E = 6\pi\eta r v_2$$
$$\Rightarrow q \times E = 6\pi\eta r(v_2 - v_1)$$
$$\Rightarrow q = \frac{6\pi\eta r(v_2 - v_1)}{E}$$

3) The results obtained confirm that the charges of the droplets are multiples
of the electronic charge, which is the charge of the electron: 1.6×10^{-19} C.
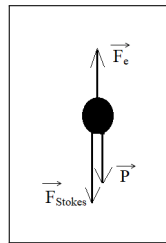
Exercise 04

1)

Figure 2.5: Immobile Phase
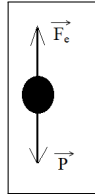
During the immobile phase;
$m \times g = q \times E$

2)

Figure 2.6: Mobile Phase

$\sum \vec{F_i} = \vec{0}$
$\Rightarrow m \times g + 6\pi\eta r v = 2qE$

We have ; $qE = m \times g \Rightarrow 2qE = 2 \times m \times g$

$\Rightarrow m \times g + 6\pi\eta r v = 2 \times m \times g$

$\Rightarrow v = \dfrac{m \times g}{6\pi\eta r v} = 21.64 \times 10^{-3} \text{ m/s}$
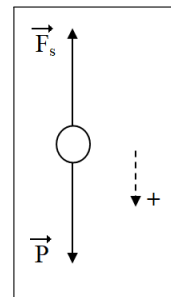
Exercise 05

a. In the absence of an electric field, there is a downward motion.
$\vec{F_s} = \vec{P}$
$\dfrac{4}{3}\pi r^3 \rho g = 6\pi\eta r v$
so; $r = \sqrt{\dfrac{18\eta v}{4\rho g}} = 1.38 \times 10^{-6}$ Angström

Calculating the mass: $\quad m = \dfrac{4}{3}\pi r^3 \rho = 9.9 \times 10^{-15}$ kg

b. The droplet is stationary when the field is created:
$\vec{F_s} = 0$
$\vec{F_E} = \vec{P}$
$\text{qE} = \text{mg} \Rightarrow \text{q} = \text{mg}(\dfrac{d}{u})$
q=4.49 $\times 10^{-19}$ Cb = 3$\times$1.6$\times 10^{-19}$ Cb
We conclude that this charge is a multiple of the elementary charge $|e| = 1.6 \times 10^{-19}$ Cb.
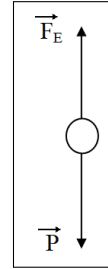
Exercise 06

a. Using the same method as the first question in the previous exercise, we deduce:
$r = 1.41 \times 10^{-6}$ m and $m = 1.06 \times 10^{-14}$ kg
$F_E = P + F_s$
$q_1 E = mg + 6\pi\eta rv$,
$$E = \dfrac{1.06 \times 10^{-14} \times 9.81 + 6 \times 3.14 \times 1.41 \times 10^{-6} \times 18 \times 10^{-6} \times 2.174 \times 10^{-4}}{6.408 \times 10^{-19}}$$
$$\boxed{E = 32.45 \times 10^4 \ V/m}$$

b. During the experiment, the droplet acquires an elementary charge
$q_2 = q_1 + |e| = 8.008 \times 10^{-19}$ C
Under the same electric field, we have:
$q_2 E = mg + 6\pi\eta rv_2 \Rightarrow v_2 = 0.76$ m/s

Exercise 07
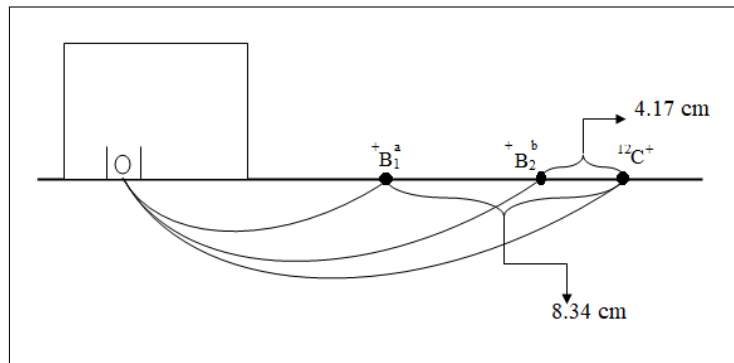
Figure 2.7: Experiment Diagram

We have;

$R_{^{12}C^+} = 24.92$ cm, and $^+B^a = B_1, ^+B^b = B_2$

$$R_{B_1} = \frac{0 \to B_1}{2} = \frac{(R_{^{12}C^+} \times 2) - 8.34}{2}$$

$$R_{B_1} = \frac{(24.92 \times 2) - 8.34}{2} = 20.75 \text{ cm}$$

$$R_{B_2} = \frac{0 \to B_2}{2} = \frac{(R_{^{12}C^+} \times 2) - 4.17}{2}$$

$$R_{B_1} = \frac{(24.92 \times 2) - 4.17}{2} = 22.84 \text{ cm}$$

1) In the velocity filter

$F_m = F_{elec} \Rightarrow \text{q} \times \text{E} = \text{q} \times \text{v} \times \text{B}$

with F_m = magnetic force, and F_{elec} = electric force, $\Rightarrow \text{V} = \dfrac{E}{B}$

2) In the analyzer

$$F_m = m \times a \Rightarrow q \times v \times B_0 = m \times \frac{v^2}{R} \text{ (m: mass)}$$

$$\Rightarrow \frac{q}{m} = \frac{v}{R \times B_0}$$

$$\Rightarrow \frac{q}{m} = \frac{E}{R \times B \times B_0}$$

$$\left. \begin{array}{l} \dfrac{q}{m_1} = \dfrac{E}{R_1 \times B \times B_0} \\ \dfrac{q}{m_2} = \dfrac{E}{R_2 \times B \times B_0} \end{array} \right\} \Rightarrow \frac{m_1}{m_2} = \frac{R_1}{R_2}$$

$$\Rightarrow \frac{m_{B_1}}{m_{C^{12}}} = \frac{R_{B_1}}{R_{C^{12}}} = \frac{20.75}{24.92}$$

$$\Rightarrow \frac{m_{B_1}}{m_{C^{12}}} = 0.83$$

$$\Rightarrow m_{B_1} = m_{C^{12}} \times 0.83$$

$$\Rightarrow \boxed{m_{B_1} = 10 \text{ a.m.u}}$$

We also have:

$$\frac{m_{B_2}}{m_{C^{12}}} = \frac{R_{B_2}}{R_{C^{12}}} = \frac{22.84}{24.92} = 0.91$$

$$\Rightarrow m_{B_2} = 12 \times 0.91$$

$$\Rightarrow \boxed{m_{B_2} = 11 \text{ a.m.u}}$$

The atomic mass of the two boron ions is $m_{B_1} = 10$ a.m.u and $m_{B_2} = 11$ a.m.u

Exercise 08

a. Knowing that 1 a.m.u (u) $= 1.66054 \times 10^{-27}$ kg:

$$m_p = \frac{1.6726 \times 10^{-27}}{1.66054 \times 10^{-27}} = 1.0073 \text{ u} \qquad\qquad m_n = \frac{1.6749 \times 10^{-27}}{1.66054 \times 10^{-27}} = 1.0087 \text{ u}$$

b. The helium nucleus $_2^4$He contains 4 nucleons: 2p+2n.

The sum of the masses of the nucleons is: $(2 \times 1.0073) + (2 \times 1.0087) = 4.032$ *a.m.u*

Deficiency in the mass of the helium nucleus:

Δm $=4.032$-4.0015=0.0305 a.m.u The cohesion energy is given by the following relation: ΔE $=(\Delta$m$)$c^2

In this relation, Δm is in kg and ΔE is obtained in J. To obtain it in eV, you need to divide the value in J by 1.602×10^{-19}. To relate ΔE to a nucleon, you then need to divide the result by 4.

$$\Delta E \text{ (ev/nucleon)} = \frac{0.00305 \times 1.66054 \times 10^{-27} \times (3 \times 10^8)^2}{1.602 \times 10^{-19} \times 4}$$

So: $\boxed{\Delta E \approx 7.1 \ MeV/nucleon}$

Exercise 09

a) Molecular weight of dichlorine, equal to twice the atomic weight of chlorine, is 71.

b) Cl**Cl** (M = 70), Cl**Cl** and **Cl**Cl (M = 72), **ClCl** (M = 74) c) Knowing the different probabilities of finding Cl (75 %) or Cl (25 %), the probabilities of finding both simultaneously being multiplicative, we get:

$\qquad (0.75)^2 = 0.562$ or 56.2 % for ClCl

$\qquad (0.25)^2 = 0.0625$ or 6.2 % for **ClCl**

$\qquad (0.75 \times 0.25) \times 2 = 0.375$ or 37.5 % for Cl**Cl**.

It can be verified that the sum of the percentages is equal to 100 %.

d) $70 \times 0.562 + 74 \times 0.0625 + 72 \times 0.375 = 71$

A value that can be determined directly from the atomic mass (35.5) of natural chlorine.

e) Mass of $AlCl_3$: $3 \times 35.5 + 27 = 133.5$.

There are four types of $AlCl_3$ molecules:

– with three Cl (M = 132) in proportion (probability) of $(0.75)^3 = 0.422$ or 42.2 %.

– with two **Cl** and one Cl (M = 134) (three equivalent combinations) in proportion of $3 \times (0.75)^2 \times 0.25 = 0.422$ or 42.2 %.

– with one Cl and two **Cl** (M = 136) (three equivalent combinations) in proportion of $3 \times 0.75 \times (0.25)^2 = 0.141$ or 14.1 %.

– with three **Cl** (M = 138) in proportion of $(0.25)^3 = 0.016$ or 1.6 %.

The sum of the percentages is equal to 100 %.

It can be verified that the weighted average of the molecular masses of the four types of molecules is equal to 133.5, in agreement with the one obtained by simply summing the atomic masses of the natural elements.

Chapter 3

Radioactivity-Nuclear Reactions

3.1 Important Concepts and Course Review

♠ **Decay and De-excitation**

Unstable nuclei spontaneously transform through decay and de-excitation, emitting radiation, both particle and electromagnetic, constituting radioactivity.

A **decay** is a transmutation, meaning the transformation of a "parent" nucleus into a "daughter" nucleus belonging to another element. It is accompanied by the emission of particles.

A **de-excitation** is the transition from an energetically excited state to the ground state. When daughter nuclei are produced in an excited state, they return to the ground state by emitting γ rays (the most energetic electromagnetic radiations, with a wavelength $\lambda < 10^{-10}$ m).

♠ **Radiations Constituting Radioactivity**

Rayonnement	α	β^-	β^+	γ
Type d'émission	noyaux d'hélium ^4_2He	électrons $^{\,\,\,0}_{-1}\text{e}$ + antineutrinos $^{0}_{0}\bar{\nu}$	positons $^{\,\,\,0}_{+1}\text{e}$ + neutrinos $^{0}_{0}\nu$	radiation électromagnétique de haute énergie
Schéma	$^A_Z\text{X} \rightarrow\, ^4_2\text{He} +\, ^{A-4}_{Z-2}\text{Y}$	$^A_Z\text{X} \rightarrow\, ^{\,\,\,0}_{-1}\text{e} +\, ^A_{Z+1}\text{Y} +\, ^{0}_{0}\bar{\nu}$	$^A_Z\text{X} \rightarrow\, ^{\,\,\,0}_{+1}\text{e} +\, ^A_{Z-1}\text{Y} +\, ^{0}_{0}\nu$	$^{A'}_{Z'}\text{Y*} \rightarrow\, ^{A'}_{Z'}\text{Y} + \gamma$

Note: β^+ type radioactivity is only observed with artificial isotopes.

♠ Time Evolution of a Radioactive Decay

A radioactive decay follows first-order kinetics: the decay rate, $-\dfrac{dN}{dt}$, is at any time t proportional to the number of radioactive atoms N present at that moment.

$$\boxed{-\frac{dN}{dt} = \lambda N}$$

λ is **the radioactive decay rate constant**, and it has the dimension: time^{-1}. It depends only on the nature of the radioactive nuclei and is independent of temperature.

The integration of the differential equation $-\dfrac{dN}{dt} = \lambda N$ between the initial time $t = 0$, where $N = N_0$, and the time t when there are N radioactive atoms remaining, leads to:

$$\boxed{\ln \frac{N_0}{N} = \lambda t}$$

or

$$\boxed{N = N_0 e^{-\lambda t}}$$

The **half-life** T is the time at which the initial number of radioactive atoms has been divided by two. The value of T is independent of N_0.

$$\boxed{T = \frac{\ln 2}{\lambda}}$$

♠ Activity of a Radioactive Source

The activity A of a radioactive source (or radioactivity) at a given time is equal to the decay rate of the radioactive nuclei it contains at that time:

$$\boxed{A = -\frac{dN}{dt} = \lambda N}$$

The unit of A is the **becquerel** (Bq); 1 Bq = 1 decay per second.

♣ Nuclear Energy

♠ Mass and Energy: Einstein's Relation

During a nuclear transformation (natural or induced), the mass of the products is always slightly less than the mass of the reactants. The mass loss is denoted Δm. Associated with this mass loss, there is a release of energy, and the value of ΔE is given by Einstein's relation:

$$\boxed{\Delta E = (\Delta m)c^2}$$

where c is the speed of light in a vacuum.

♠ Binding Energy of a Nucleus

The mass of an atomic nucleus is always slightly less than the sum of the masses of its nucleons. The difference Δm between the mass of the nucleons and that of the nucleus is called the mass defect. The corresponding amount of energy ΔE is the energy that would be released if the nucleus formed from the nucleons.

A nucleus is more stable when this quantity ΔE is larger. That's why ΔE is called the **cohesion energy** (or **binding energy**) of the nucleus. To compare the stabilities of nuclei of different elements, we compare the binding energies per nucleon, expressed in MeV/nucleon[2].

$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$; $1 \text{ MeV} = 1.602 \times 10^{-19} \times 10^{6} = 1.602 \times 10^{-13} \text{ J}$

3.2   Exercise Statements

Exercise 01

The first stage of the radioactive decay of $^{238}_{92}\text{U}$ leads to $^{234}_{90}\text{Th}$.

1. Write the reaction for this radioactive decay.

2. Calculate the energy accompanying this radioactive decay in joules and electron-volts.

3. Calculate the activity (in decays per second, d.p.s, and Curie) of 1 gram of $^{238}_{92}\text{U}$.
   <u>Given</u>: h (Planck's constant) $= 6.626 \times 10^{-34}$ J.s^{-1};
   c (speed of light) $= 3 \times 10^8$ m.s^{-1}; $W_H = \pm 13.6$ eV; $^{238}\text{U} = 238.0508$ atomic mass units (a.m.u);
   $^{234}\text{Th} = 234.0437$ a.m.u; X $= 4.0026$ a.m.u; half-life of ^{238}U; T $= 4.5 \times 10^9$ years.

Exercise 02

Phosphorus ^{32}P is used as a radioactive tracer in the detection of certain tumors. This element is a β^- emitter with a half-life of 14.2 days. Cellular preparations labeled with ^{32}P have an activity of 1.6 mCi. Calculate the duration of use of these preparations, knowing that they are discarded when their activity is reduced to 10 μCi. (Note that 1 Ci = 37 GBq.)

Exercise 03

The element gallium Ga (Z = 31) has two stable isotopes, ^{69}Ga and ^{71}Ga.
1- Determine the approximate values of their natural abundances, knowing that the atomic molar mass of gallium is 69.72 g/mol.
2- Why is the result only approximate?
3- There are three radioactive isotopes of gallium, ^{66}Ga, ^{72}Ga, and ^{73}Ga. Predict the type of radioactivity for each one and write the corresponding reaction.

^{69}Ga: 31 protons and 38 neutrons - Stable isotope
^{71}Ga: 31 protons and 40 neutrons - Stable isotope

Exercise 04

I. The half-life of a radioactive sample is 3×10^5 years. Calculate the value of its radioactive constant λ. After what duration has the initial quantity of radioactive nuclei been divided by 8?
II. The half-life of a radioactive source composed of a mass m = 100 g of radioactive nuclei is $T_{1/2} = 2400$ hours. Calculate the mass of remaining radioactive nuclei after one year. A radioactive source with a half-life of 65 years has 1.256×10^{21} radioactive nuclei at a given time. Calculate the activity of this source at that time.

III. A Geiger-Müller counter, placed near a radioactive sample, detects an average of 1000 decays per minute. 12 hours later, placed under the same conditions, it detects an average of 320 decays per minute. What is the half-life of the radioactive nuclei?

Exercise 05

On April 26, 1986, a reactor at the Chernobyl nuclear power plant went out of control and exploded. The plume released into the atmosphere dispersed significant radioactive elements, such as iodine-131 and cesium-137, which had significant health implications. Iodine-131 has a half-life of 8 days and is a β^- emitter.

Recall the definition of half-life.

Calculate the radioactive constant λ and the time constant τ for the decay of iodine-131.

The activity A_0 of iodine-131 released by the Chernobyl explosion is estimated to be 1760 PBq (1 PBq = 10^3 TBq = 10^6 GBq). Express its current activity A, 32 years later. Explain the distribution of iodine-127 (in the form of potassium iodide) to populations living near nuclear power plants in case of a nuclear accident.

Data: 1 PBq = 10^{15} Bq; 1 Bq = 2.7×10^{-11} Ci; 1 Ci = 3.7×10^{10} d.p.s.

Exercise 06

I. The decay period of carbon-14 is 5.7×10^3 years.

Calculate the time required for 75% of it to decay using two methods.

II. The activity of one gram of carbon at a given moment is 15.3 decays per minute. Knowing that the period is 5600 years, calculate:

1. The number of nuclei and the remaining mass of carbon.

2. The remaining percentage of carbon.

Exercise 07

Salts of radioactive phosphorus ^{32}P have an activity $A_1 = 5$ microcurie at time t_1. This activity becomes equal to $A_2 = 3.08$ microcurie ten days later.

1. Determine the radioactive constant and the period of phosphorus.

2. With t_1 being equal to 14.3 days, calculate the initial activity A_0 of the salts.

3. Calculate the initially present mass m_0.

Exercise 08

Positron emission tomography (PET) is a functional medical imaging method that takes advantage of the annihilation of positrons emitted by a radioactive tracer that accumulates in the target organ.

Annihilation occurs due to a collision with an electron in the medium, happening at a very close distance to the tracer (less than 1 mm), and is accompanied by the emission of two photons. Observing these photons with a suitable camera allows the detection of tracer concentration sites in the organ.

One of the main tracers used is ^{18}fluorodeoxyglucose (^{18}FDG), which is injected into the patient intravenously. This tracer binds to tissues that consume sugars, such as cancerous tumors or the brain, for example.

a) ^{18}F is produced by bombarding ^{18}O with protons. Write the corresponding reaction. Then, write the decay of ^{18}F with positron emission, followed by the annihilation process.

b) Knowing that ^{18}F decays 90% in 366 minutes, calculate the half-life and draw a conclusion.

Exercise 09

Tritium is primarily found as tritiated water (^{3}H$_2$O) in the natural environment, as well as in living species. Naturally produced by cosmic rays acting on nitrogen, oxygen, and argon in the air, it integrates into the normal water cycle.

In the event of nuclear contamination (explosions, emissions from nuclear reactors, releases from reprocessing plants), the tritium content in water increases. Environmental monitoring includes monitoring the tritium content in natural waters.

a) Write the nuclear decay reaction of tritium, knowing that it is a β^- emitter. What does this transformation amount to?

b) An analysis showed that a river water sample contains one tritium atom per 10^{19} atoms of ordinary hydrogen.

The half-life of tritium is 12.3 years. What will be the proportion of tritium 50 and 100 years after the sample was taken, assuming that tritium cannot be regenerated during storage?

c) In the event of contamination, how long does it take for the tritium activity to be only one-thousandth of its initial activity?

3.3   Exercise Solutions

Exercise 01

1. The radioactive decay reaction is: $^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$

2. To calculate the decay energy, we use Einstein's relation:
   $\Delta E = \Delta m \times c^2$
   Now, $\Delta m = m_{Th} + m_{He} - m_U = 234.0437 + 4.0026 - 238.0508$
   $\Delta m = -0.0045$ atomic mass units (a.m.u)
   So: $\Delta m = \dfrac{-0.0045 \times 10^{-3}}{6.023 \times 10^{23}} \times (3 \times 10^8)^2 = -0.672 \times 10^{-10}$ joules
   Now, 1 eV $= 1.6 \times 10^{-19}$,
   we obtain: $\Delta E = \dfrac{-0.672 \times 10^{-10}}{1.6 \times 10^{-19}} = -0.42 \times 10^9$ eV = -0.42 MeV

3. $A = \lambda \times N = \dfrac{\ln 2}{T} \times N$ where N is the number of remaining nuclei at time t.
   $N = \dfrac{\mathscr{N}}{238} = \dfrac{6.023 \times 10^{23}}{238} = 0.025 \times 10^{23}$ nuclei.
   We obtain: $A = \dfrac{\ln 2}{4.5 \times 10^9 \times 365 \times 24 \times 3600} \times 0.025 \times 10^{23} = 1.22 \times 10^4$ d.p.s
   Now, 1 Ci $= 3.7 \times 10^{10}$ d.p.s, so $A = \dfrac{1.22 \times 10^4}{3.7 \times 10^{10}} = 0.33 \times 10^{-6}$ Ci

Exercise 02

We have: $A_0 = \exp(-\lambda \times t)$
$\Rightarrow t = \dfrac{-1}{\lambda \ln(\dfrac{A}{A_0})}$
$\Rightarrow t = -T \times \ln \dfrac{(\dfrac{A}{A_0})}{\ln 2}$
Now, 1 mCi $= 10^{-3}$ Ci and 1 μCi $= 10^{-6}$ Ci

$$\Rightarrow t = -14.2 \times \ln \dfrac{(\dfrac{10 \times 10^{-6}}{1.6 \times 10^{-3}})}{\ln 2} = 72$$

The duration of use of the preparations is 72 days.

Exercise 03

1. The two isotopes of gallium Ga (Z=31) are denoted (1) for ^{69}Ga and (2) for ^{71}Ga.

M = $x_1 M_1 + x_2 M_2$ with $M_1 \approx A_1 = 69$ and $M_2 \approx A_2 = 71$

$69.72 = 69x_1 + 71x_2$ $x_1 + x_2 = 1$

$\Rightarrow 69.72 = 69x_1 + 71(1\text{-}x_1)$

$x_1 = 0.64$ and $x_2 = 0.36$

$\Rightarrow 64\%$ ^{69}Ga and 36% ^{71}Ga.

2. Natural elements are composed of multiple isotopes in different proportions. Since the molar mass is the sum of these molar proportions, it cannot be an integer. It is not strictly equal to the mass number because the latter is an integer for each isotope.

Exercise 04

I

• The value of the radioactive constant λ

$\lambda = \dfrac{\ln(2)}{T_{1/2}} = 1.8 \times 10^{-6}$ years^{-1}.

• The half-life of a radioactive sample is 3.8×10^5 years. After 3 half-lives, 1.14×10^6 years, the initial quantity is divided by 2^3.

II

• We use the radioactive decay law $m(t) = m_0 \exp(-\lambda t)$.

The radioactive constant is $\lambda = \dfrac{\ln(2)}{T_{1/2}} = 2.9 \times 10^{-4}$ h^{-1} = 2.54 years^{-1}.

At time $t = 0$, the mass of radioactive nuclei is $m_0 = 100$ g

At time $t = 1$ year, we have:

$$100 \exp(-2.54 \times 1) = 7.9 \text{ g}$$

III

The number of nuclei at time t is $N(t) = 1.256 \times 10^{21}$ nuclei.

$A(t) = (\ln 2 / t_{1/2}) N(t) = 1.340 \times 10^{19}$ decays per year $= 4.2 \times 10^{11}$ Bq.

IV

At time $t = 0$, $A_0 = 1000$ d.p.m. At time $t = 12$ h, we have $A(t) = 320$ d.p.s. The radioactive decay law allows us to write:

$$\lambda = (-1/t) \ln(A(t)/A_0)$$

and

$$T_{1/2} = (-\ln(2)t)/\ln(A(t)/A_0) = 7.3h$$

Exercise 05

- Definition of half-life: Half-life is the duration after which the number of radioactive nuclei is divided by 2 through decay.

- Radioactive constant $\lambda = (\ln 2)/(T_{1/2}) = 31.624 \text{ years}^{-1} = 8.664\times10^{-2}$ $\text{J}^{-1} = 10^{-6}\text{s}^{-1}$

- Time constant $\tau = 10^6$ s, which is 11.5 days.

- Expression of activity 32 years later:

$$\left. \begin{array}{l} 1\,d.p.s = 1Bq \\ 1PBq = 10^{15}PBq \end{array} \right\} \Longrightarrow 1760PBq = 1760{\times}10^{15}Bq = 1760{\times}10^{15}\,d.p.s$$

According to the exponential law: $A = A_0 \exp(-\lambda t)$
$\Longrightarrow A = 1760 \times 10^{15} \exp(-31.624 \times 32\,years)$

- Iodine-131, like iodine-127, binds to the thyroid gland. There is therefore a danger for neighbors of nuclear power plants in the event of an accident. To avoid this danger, non-radioactive iodine-127 is ingested at a dose such that the thyroid gland becomes saturated. This gland no longer binds radioactive iodine-131.

Exercise 06
I Method 1
$$A = \lambda N = \frac{-dt}{t} \Rightarrow T = \frac{\ln 2}{\lambda}$$
$$\Rightarrow \lambda = \frac{0.96}{5.7 \times 10^3 \times 365 \times 24 \times 3600}$$
$$\Rightarrow \lambda = 3.85 \times 10^{-12}\ s^{-1}$$

$$\begin{cases} \text{at } t_0 \Longrightarrow N_0 = 100\% \\ \text{at } t \Longrightarrow N_t = 100\% - 75\% \end{cases}$$

$$N_t : \text{number of remaining nuclei}$$

$$N_t = N_0 \times (1 - 0.75) = 0.25 N_0$$

$$N_t = 0.25 N_0 = \frac{1}{4} N_0$$

$$\frac{1}{4} N_0 = N_0 \exp(-\lambda t) \Rightarrow \frac{1}{4} = \exp(-\lambda t)$$

$$\Rightarrow \ln \frac{1}{4} = -\lambda t$$

$$\Rightarrow \ln 4 = \lambda t$$

$$\Rightarrow t = \frac{\ln 4}{\lambda} = \frac{\ln 4}{3.85 \times 10^{-12}}$$

$$\Rightarrow \boxed{t = 3.61 \times 10^{11}}$$

Method 2

$$\ln 4 = \lambda t \Rightarrow \ln 4 = \frac{\ln 2}{T} \times t$$
$$t = \frac{\ln 4}{\ln 2} \times T \Rightarrow \boxed{t = 2T}$$

II

A = 15.3 d.p.m $\Rightarrow A = \dfrac{15.3}{60} = 0.255$ d.p.s

T=5600 years $\Rightarrow \lambda = \dfrac{\ln 2}{T} = \dfrac{0.69}{5600 \times 365 \times 24 \times 3600}$

$\Rightarrow \lambda = 3.96 \times 10^{-12} \text{ s}^{-1}$

We have 1 Ci = 3.96×10^{10} d.p.s

A = $\lambda N_t \rightarrow N_t = \frac{A_t}{\lambda} \rightarrow N_t = \dfrac{0.225}{3.96 \times 10^{-12}} = 6.439 \times 10^{10}$

The number of remaining nuclei is equal to 6.439×10^{10}

The remaining percentage in carbon :

We have 1 mole = $\mathcal{N}$ nuclei

$$\begin{cases} 6.023 \times 10^{23} \rightarrow 14 \times 10^{-3} \ kg \\ \\ 6.439 \times 10^{10} \rightarrow x \ ? \ \text{(mass)} \end{cases}$$

$$x = \frac{6.439 \times 10^{10} \times 14 \times 10^{-3}}{6.023 \times 10^{23}}$$

$$x = 14.97 \times 10^{-16} \text{ kg}$$

$$\begin{cases} 1 \times 10^{-3} \to 100\% \\ \\ 14.97 \times 10^{-16} \to \alpha(\text{percentage}) \end{cases} \Longrightarrow \alpha = \frac{14.97 \times 10^{-16} \times 100}{10^{-3}} \Rightarrow \boxed{\alpha = 14.97 \times 10^{-11}\%}$$

Exercise 07

We have; $A_1 = 5 \ \mu\text{Ci}$ at t_1 and $A_2 = 3.08 \ \mu\text{Ci}$ at t_2 with $t_2 = 10$ days $+t_1$.

1) We have;
$$\begin{cases} N_1 = N_0 \exp(-\lambda t_1) \\ N_2 = N_0 \exp(-\lambda(t_1 + 10)) \end{cases}$$

$$\Rightarrow \begin{cases} \lambda N_1 = \lambda N_0 \exp(-\lambda t_1) \\ \lambda N_2 = \lambda N_0 \exp(-\lambda(t_1 + 10)) \end{cases}$$

$$\Rightarrow \begin{cases} A_1 = A_0 \exp(-\lambda t_1) \\ A_2 = A_0 \exp(-\lambda(t_1 + 10)) \end{cases}$$

$$\Rightarrow \begin{cases} \dfrac{A_1}{A_2} = \dfrac{\exp(-\lambda t_1)}{\exp[-\lambda(t_1 + 10)]} = \dfrac{1}{\exp(-\lambda 10 \text{ days})} \end{cases} \Rightarrow \{\dfrac{A_1}{A_2} = \exp(\lambda 10 \text{ days})$$

$$\text{Hence, } \ln \frac{A_1}{A_2} = \lambda 10 \text{ days}$$

$$\lambda = \frac{1}{10 \text{ days}} \times \ln \frac{A_1}{A_2}$$

$$\Rightarrow \boxed{\lambda = 0.049 \text{ day}^{-1}} \ , \ (\lambda \text{ is the radioactive constant})$$

$$\text{The period } T_{1/2} = \frac{\ln 2}{\lambda} = 14 \text{ days}^{-1}$$

2)

$$t_1 = 14.3 \text{ days}$$
$$\Rightarrow A_1 = A_0 \exp(-\lambda t_1) \Rightarrow A_0 = A_1 \exp(\lambda t_1)$$
$$\text{We have } A_1 = 5 \ \mu\text{Ci} = 5 \times 10^{-6} \text{ Ci}$$
$$\Rightarrow A_0 = 5 \times 10^{-6} \exp(0.049 \times 14.3)$$
$$\Rightarrow \boxed{A_0 = 10.07 \times 10^{-6} \text{ Ci}}$$

3) $A_0 = \lambda N_0 \Rightarrow N_0 = \dfrac{A_0}{\lambda}$ (Where N_0 is the initial number of nuclei)
We need to make some conversions:

$$If \ 1 \text{ Ci} = 3.7 \times 10^{10} \text{ d.p.s}$$

$$\text{and } 1 \text{ d.p.d} = \frac{1}{3.7 \times 10^{10}} = 2.70 \times 10^9 \text{ Ci}$$

$$10.07 \times 10^{-6} \text{ Ci} = 3.72 \times 10^{-15} \text{ d.p.d}$$

$$N_0 = \frac{3.72 \times 10^{-15}}{0.049} = 75.91 \times 10^{-15} \text{ nuclei}$$

$$\Rightarrow m_0 = \frac{75.91 \times 10^{-15} \times (32 \text{ g})}{6.023 \times 10^{23}} = 40.33 \times 10^{-39} \text{ g}$$

$$\boxed{m_0 = 40.33 \times 10^{-39} \text{ g}}$$

Note: We used the disintegration per day because λ is in day^{-1}. It is also possible to use Ci and d.p.s.

Exercise 08
a) Knowing that the atomic number of fluorine is 9, the production reaction of ^{18}F is:
$$^{18}_{8}\text{O} + ^{1}_{1}\text{H} \longrightarrow ^{18}_{9}\text{F} + ^{1}_{0}\text{n}$$
Its decay with the emission of a positron is:
$$^{18}_{9}\text{F} \longrightarrow ^{18}_{8}\text{O} + ^{0}_{+1}\text{e} + ^{0}_{0}\nu$$
Representing the photon as $^{0}_{0}\gamma$, the annihilation of a positron by collision with an electron in the medium is written as:
$$^{0}_{+1}\text{e} + ^{0}_{-1}\text{e} \longrightarrow 2^{0}_{0}\gamma$$
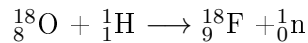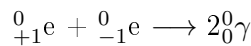
b) By eliminating λ between the relations ($\ln \dfrac{N_0}{N} = \lambda t$) and ($T_{1/2} = \dfrac{\ln 2}{\lambda}$), we obtain:
$$T_{1/2} = t \times \frac{\ln 2}{\ln(N_0/N)}$$
where N_0/N represents the inverse of the remaining fraction of radioactive species at time t considered.
At $t=366$ min, ^{18}F has decayed to 90%; 10% remains, so $N_0/N = 10$.

$$\text{T} = 366 \times \frac{\ln 2}{\ln 10} = 110.2 \Rightarrow \boxed{T_{1/2} \approx 110 \text{ min}}$$

Conclusion: ^{18}F has a short half-life (less than 2 hours), which allows for its rapid elimination. This parameter is important for all tracers used in medical applications, so that patients do not suffer harm.

Exercise 09
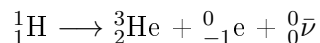
a)
$$^1_1\text{H} \longrightarrow {}^3_2\text{He} + {}^0_{-1}\text{e} + {}^0_0\bar{\nu}$$
This transformation can be summarized as the transformation of a neutron into a proton, as follows:
$$^1_0\text{n} \longrightarrow {}^1_1\text{p} + {}^0_{-1}\text{e} + {}^0_0\bar{\nu}$$
b) Tritium is present in trace amounts; at the time of collection, its content (in %) relative to ordinary hydrogen is:
$$p_0 = \frac{1 \times 100}{10^{19}} = 10^{-17}\%$$
which corresponds to an initial quantity of N_0 atoms.
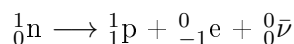
At a time t during storage, the quantity N of remaining atoms is deduced as follows:
$$N = N_0 e^{-\lambda t} = N_0 e^{(\frac{t}{T_{(1/2)}})\ln 2}$$
The corresponding proportion p of remaining tritium is therefore written as:
$$p = p_0 \exp(\frac{t}{T_{1/2}})\ln 2$$
$\Rightarrow$ $T_{(1/2)}$=12.3 years; $p_0 = 10^{-17}\%$

- $t = 50$ years $\boxed{p = 6.0 \times 10^{-19}\%}$

- $t = 100$ years $\boxed{p = 3.6 \times 10^{-20}\%}$

c) The activity at time t is the rate of decay: $A = \lambda N$. The proportionality between A and N allows us to write:
$$\frac{A}{A_0} = \frac{N}{N_0} = \exp -\lambda t = \exp\left(\frac{t}{T_{1/2}}\right)\ln 2$$
Hence:
$$t = -\frac{T_{(1/2)}}{\ln 2} \times \ln \frac{A}{A_0}$$
When T=12.3 years ; A/A_0=1/1000= 10^{-3}
$$t = -\frac{12.3}{\ln 2} \times \ln 10^{-3}, \text{ therefore: } \boxed{T = 122.6 \; years}$$

3.4 Problems

Problem 01

The half-life of Zn-71 is 2.4 minutes. If one had 100.0 g at the beginning, how many grams would be left after 7.2 minutes has elapsed ?

Solution

7.2 / 2.4 = 3 half-lives

(1/2)3 = 0.125 (the amount remaining after 3 half-lives)

100.0 g x 0.125 = 12.5 g remaining

Problem 02

Pd-100 has a half-life of 3.6 days. If one had 6.02 x 1023 atoms at the start, how many atoms would be present after 20.0 days?

Solution

20.0 / 3.6 = 5.56 half-lives

$(1/2)^{5.56}$ = 0.0213 (the decimal fraction remaining after 5.56 half-lives)

(6.02 x 1023) (0.0213) = 1.28 x 1022 atoms remain

Problem 03

Os-182 has a half-life of 21.5 hours. How many grams of a 10.0 gram sample would have decayed after exactly three half-lives?

Solution

$(1/2)^3$ = 0.125 (the amount remaining after 3 half-lives)

10.0 g x 0.125 = 1.25 g remain

10.0 g - 1.25 g = 8.75 g have decayed

Note that the length of the half-life played no role in this calculation. In addition, note that the question asked for the amount that decayed, not the amount that remaning.

Problem 04

After 24.0 days, 2.00 milligrams of an original 128.0 milligram sample remain. What is the half-life of the sample?

Solution

The decimal fraction remaining:

2.00 mg / 128.0 mg = 0.015625

2) How many half-lives must have elaspsed to get to 0.015625 remaining?

$(1/2)^n$ = 0.015625

n log 0.5 = log 0.015625

n = log 0.5 / log 0.015625

n = 6

3) Determine the half-life:

24 days / 6 half-lives = 4.00 days

Problem 05

A radioactive isotope decayed to 17/32 of its original mass after 60 minutes. Find the half-life of this radioisotope.

Solution

17/32 = 0.53125 (this is the decimal amount that remains)

$(1/2)^n = 0.53125$

n log 0.5 = log 0.53125

n = 0.91254 (this is how many half-lives have elapsed)

60 min / 0.91254 = 65.75 min

n = 66 min (to two sig figs)

Problem 06

How long will it take for a 40.0 gram sample of I-131 (half-life = 8.040 days) to decay to 1/100 its original mass?

Solution

$(1/2)^n = 0.01$

n log 0.5 = log 0.01

n = 6.64

6.64 x 8.040 days = 53.4 days

Problem 07

Fermium-253 has a half-life of 0.334 seconds. A radioactive sample is considered to be completely decayed after 10 half-lives. How much time will elapse for this sample to be considered gone?

Solution

0.334 x 10 = 3.34 seconds

Problem 08

At time zero, there are 10.0 grams of W-187. If the half-life is 23.9 hours, how much will be present at the end of one day? Two days? Seven days?

Solution

24.0 hr / 23.9 hr/half-life = 1.0042 half-lives

One day = one half-life; $(1/2)^{1.0042} = 0.4985465$ remaining = 4.98 g

Two days = two half-lives; $(1/2)^{2.0084} = 0.2485486$ remaining = 2.48 g

Seven days = 7 half-lives; $(1/2)^{7.0294} = 0.0076549$ remaining = 0.0765 g

Problem 09

100.0 grams of an isotope with a half-life of 36.0 hours is present at time zero. How much time will have elapsed when 5.00 grams remains?

Solution

5.00 / 100.0 = 0.05 (decimal fraction remaining)

$(1/2)^n = 0.05$

n log 0.5 = log 0.05

n = 4.32 half-lives

36.0 hours x 4.32 = 155.6 hours

Problem 10

How much time will be required for a sample of H-3 to lose 75% of its radioactivity? The half-life of tritium is 12.26 years.

Solution

If you lose 75%, then 25% remains. Use 0.25 rather than 25%.

$(1/2)^n = 0.25$

n = 2 (remember $(1/2)^n = 1/4$ and $1/4 = 0.25$)

12.26 x 2 = 24.52 years

Comment: the more general explanation follows:

$(1/2)^n = 0.25$

n log 0.5 = log 0.25

n = log 0.25 / log 0.5

n = 2

Problem 11

The half life of iodine-131 is 8.040 days. What percentage of an iodine-131 sample will remain after 40.20 days?

Solution

40.20 d / 8.040 d = 5

$(1/2)^5 = 0.03125$

percent remaining = 3.125%

Problem 12

The half-life of thorium-227 is 18.72 days How many days are required for three-fourths of a given amount to decay?

Solution

$3/4 = 0.75 \leftarrow$ amount decayed

$1 - 0.75 = 0.25 \leftarrow$ amount remaining

$(1/2)^n = 0.25$

n = 2

(18.72 day) (2) = 37.44 day

Problem 13

If you start with 5.32 x 10^9 atoms of Cs-137, how much time will pass before the amount remaining is 5.20 x 10^6 atoms? The half-life of Cs-137 is 30.17 years.

Solution

5.20 x 10^6 / 5.32 x 10^9 = 0.0009774436 (the decimal amount remaining)

$(1/2)^n = 0.0009774436$

n log 0.5 = log 0.0009774436

n = 9.99869892 half-lives

(30.17 yr) (10) = 301.7 yr

Problem 14

The half-life of the radioactive isotope phosphorus-32 is 14.3 days. How long until a sample loses 99% of its radioactivity?

Solution

99% loss means 1% remaining

1% = 0.01

$(1/2)^n = 0.01$

n log 0.5 = log 0.01

n = 6.643856

(14.3 day) (6.643856) = 95.0 day

Problem 15

The half-life of palladium-100 is 4 days. After 12 days a sample of Pd-100 has been reduced to a mass of 4.00 mg. (a) Determine the starting mass. (b) What is the mass 8 weeks after the start?

Solution

12 day / 4 day = 3

$(1/2)^3 = 0.125$

4.00 mg / 0.125 = 32.0 mg

8 weeks = 56 days

56 d / 4 = 14 half-lives

$(1/2)^{14} = 0.000061035$

(32.0 mg) (0.000061035) = 0.00195 mg (rounded to three figs)

Problem 16

Rn-222 has a half-life of 3.82 days. How long before only 1/16 of the original sample remains?

Solution

recognize 1/16 as a fraction associated with 4 half-lives (from $1/2^4 = 1/16$)

3.82 days x 4 = 15.3 days

Problem 17

One-eighth of a radioactive sample remains 9 days after it was brought into the lab. What is the half-life?

Solution

One-eighth is evocative of three half-lives.

9 day / 3 = 3 day **Problem 18**

A sample of Se-83 registers 10^{12} disintegrations per second when first tested. What rate would you predict for this sample 3.5 hours later, if the half-life is 22.3 minutes? **Solution**

210 min / 22.3 min = 9.42 half-lives (210 min is 3.5 hours)

$(1/2)^{9.42} = 0.00146$ (the decimal fraction remaining)

10^{12} x 0.00146 = 1.46 x 10^9 disintegrations per second remaining

Problem 19

Iodine-131 has a half-life of 8.040 days. If we start with a 40.0 gram sample, how much will remain after 24.0 days?

Solution

24.0 days / 8.040 days = 2.985 half-lives

$(1/2)^{2.985} = 0.1263$ (the decimal fraction remaining)

40.0 g x 0.1263 = 5.05 g

Problem 20

If you start with 2.97 x 10^{22} atoms of molybdenum-99 (half-life = 65.94 hours), how many atoms will remain after one week?

Solution

one week = 168 hours

168 / 65.94 = 2.548

$(1/2)^{2.548}$ = 0.171 (the decimal fraction remaining)

(2.97 x 10^{22}) x 0.171 = 5.08 x 10^{21}

Problem 21

The isotope H-3 has a half life of 12.26 years. Find the fraction remaining after 49 years.

Solution

49 / 12.26 = 3.9967

$(1/2)^{3.9967}$ = 0.0626

Problem 22

How long will it take for a 64.0 g sample of Rn-222 (half-life = 3.8235 days) to decay to 8.00 g?

Solution

8.00 / 64.0 = 0.125 (the decimal fraction remaining)

$(1/2)^{n}$ = 0.125

by experience, n = 3 (remember that 0.125 is 1/8)

3.8235 x 3 = 11.4705 days

Problem 23

What percentage of the parent isotope remains after 0.5 half lives have passed?

Solution

$(1/2)^{n}$ = decimal amount remaining

where n = the number of half-lives

$(1/2)^{0.5}$ = 0.707

The question asks for a percentage, so 70.7%

Problem 24

A scientist needs 10.0 micrograms of Ca-47 (half-life = 4.50 days) to do an experiment on an animal. If the delivery time is 50.0 hours, how many micrograms of $^{47}CaCO_3$ must the scientist order?

Solution

4.50 days x 24 hrs/day = 108 hrs

50/108 = 0.463 half-lives

$(1/2)^{0.463}$ = 0.725 (the decimal portion of Ca-47 remaining after 50 hrs)

10.0 mg / 0.725 = 13.8 mg

Problem 25

Manganese-56 has a half-life of 2.6 h. What is the mass of manganese-56 in a 1.0 g sample of the isotope at the end of 10.4 h?

Solution

10.4 / 2.6 = 4

4 half-lives = 0.0625 remaining

0.0625 g

Problem 26

The half life in two different samples, A and B, of radio-active nuclei are related according to T(1/2,B) = T(1/2,A)/2. In a certain period the number of radio-active nuclei in sample A decreases to one-fourth the number present initially. In the same period the number of radio-active nuclei in sample B decreases to a fraction f of the number present initially. Find f.

Solution

a) Sample A underwent two half-lives:

$$1 \rightarrow 1/2 \rightarrow 1/4$$

b) Let us set the length of one half-life of A equal to 1. Therefore the total amount of elapsed time for A was 2.

T(1/2,B) = T(1/2,A)/2

Since T(1/2,A) = 1,

we now know that T(1/2,B) = 1/2

c) Allow B to go through several half-lives such that the total amount of time = 2. This is 4 half-lives (1/2 + 1/2 + 1/2 + 1/2 = 2):

Four half-lives: $1 \rightarrow 1/2 \rightarrow 1/4 \rightarrow 1/8 \rightarrow 1/16$

f = 1/16

Problem 27

You have 20.0 grams of P-32 that decays 5% daily. How long will it take for half the original to decay?

Solution

In 24 hours, the sample goes from 100% to 95%

$(1/2)^n = 0.95$

n log 0.5 = log 0.95

n = 0.074

24 hrs / 0.074 = 324 hrs (one half-life)

Problem 28

A sample of radioactive isotopes contains two different nuclides, labeled A and B. Initially, the sample composition is 1:1, i.e., the same number of nuclei A as nuclei B. The half-life of A is 3 hours and, that of B, 6 hours. What is the expected ratio A/B after 18 hours?

Solution

A has a half-life of 3 hrs, so 18 hrs = 6 half-lives.

B has a half-life of 6 hrs, so 18 hrs = 3 half-lives.

After 6 half lives, the fraction of A left is $1/(2^6) = 1/64$

The fraction of B left is $1/(2^3) = 1/8$.

Since A/B started out at 1/1, A/B at 18 hrs = (1/64) / (1/8) = 1/8. This could also be expressed as: 0.5^6 / 0.5^3 = 0.5^{6-3} = 1/8

Problem 29

The ratio of tritium, H-3, to hydrogen, H-1, in a sample of water was $1:1 \times 10^{19}$. If the half life of tritium is 12.25 years, calculate the actual number of tritium atoms remaining in 10.0 g water after a period of 49 years.

Solution

1) Moles, then molecules of water:

10.0 g / 18.0148 g/mol = 0.555099 mol
(0.555099 mol) (6.02214 x 10^{23} molecules / mol) = 3.342884 x 10^{23} molecules

2) Atoms of hydrogen in 10.0 g of water:
(2 atoms/molecules) (3.342884 x 10^{23} molecules) = 6.685768 x 10^{23} atoms

3) Atoms of H-3:
6.685768 x 10^{23} / 1 x 10^{19} = 66858 atoms of H-3 (to the nearest whole number)

4) Half-lives elapsed:
49 yr / 12.25 yr = 4

5) Amount remaining after 4 half-lives:
$(1/2)^4$ = 1/16 = 0.0625

6) atoms remaining after 4 half-lives:
(66858 atoms) (0.0625) = 4179 atoms (to the nearest whole number)

Problem 30

The isotope Ra-226 decays to Pb-206 in a number of stages which have a combined half-life of 1640 years. Chemical analysis of a certain chunk of concrete from an atomic-bombed city, preformed by an archaeologist in the year 6264 AD, indicated that it contained 2.50 g of Ra-226 and 6.80 g of Pb-206. What was the year of the nuclear war?

Solution

Start by ignoring a few chemical realities and assume all the Ra-226 ends up as lead.

a) Calculate moles of Ra-226 decayed:
6.80 g / 205.974465 g/mol = 0.033013801 mol of Pb-206 decayed
0.033013801 mol of Ra-226 decayed

b) Calculate grams of Ra-226 initially present:
(0.033013801 mol) (226.02541 g/mol) = 7.462 g of Ra-226 decayed

7.462 + 2.50 = 9.962 g of Ra-226 initially present

    c) Calculate decimal fraction of Ra-226 remaining:
2.50 g / 9.962 g = 0.251

    d) Calculate number of half-lives elapsed:
$(1/2)^n = 0.251$
n = 2

    e) Calculate year of war:
1640 x 2 = 3280 y elapsed since war
6264 - 3280 = 2984 AD

Problem 31

A radioactive sample contains 3.25×10^{18} atoms of a nuclide that decays at a rate of 3.4×10^{13} disintegrations per 26 min.

    (a) What percentage of the nuclide will have decayed after 159 days?
(b) What is the half-life of the nuclide?

Solution

Solution to a:

    159 days x 24 hrs/day x 60 min/hour = 228960 min
228960 min x (3.4×10^{13} disintegrations per 26 min) = $2.994 \times 10 \times 10^{17}$ total dis in 159 days
$2.994 \times 10 \times 10^{17}$ / 3.25×10^{18} = 0.0921
9.21% has disintegrated.

Solution to b:

    0.9079 is the decimal fraction of the substance remaining since 0.0921 has gone away
$(1/2)^n = 0.9079$
n log 0.5 = log 0.9079
n = 0.139 half-lives
159 day / 0.139 = 1144 days

Problem 32

The radioisotope potassium-40 decays to argon-40 by positron emission with a half life of 1.27×10^9 yr. A sample of moon rock was found to contain 78 argon-40 atoms for every 22 potassium-40 atoms. What is the age of the rock?

Solution

Assume the sample was 100% K-40 at start. In the present day, the sample contains 78% Ar-40 and 22% K-40. We will use 0.22, the decimal percent of K-40 remaining:
$(1/2)^n = 0.22$
where n is the number of half-lives. n log 0.5 = log 0.22
n = 2.18

What is the total elapsed time?

(2.18) (1.27 x 10^9) = 2.77 x 109 yrs

Problem 33

What is the age of a rock in which the mass ratio of Ar-40 to K-40 is 3.8?
K-40 decays to Ar-40 with a half-life of 1.27 x 10^9 yr.

Solution

Since, the sample is 3.8 parts by mass Ar and 1 part K, the orginal sample contained 4.8 parts K and zero parts Ar.

What is the decimal amount of K-40 that remains?

1 part divided by 4.8 parts = 0.20833

How many half-lives are required to reach 0.20833 remaining? $(1/2)^n = 0.20833$

where n is the number of half-lives.

n log 0.5 = log 0.20833

n = 2.263

What is the total elapsed time?

(2.263) (1.27 x 10^9) = 2.87 x 10^9 yrs

Problem 34

A radioactive isotope has a half-life of 4.5 days. What fractions of the sample will exist after 9 and 18 days?

(a) 1/2 and 1/4 of the original amount

(b) 1/9 and 1/18 of the original amount

(c) 1/4 and 1/16 of the original amount

(d) 1/4 and 1/8 of the original amount

Solution

$Half-lives\ elapsed$	$zero$	one	two	$three$	$four$
$Days\ elapsed$	0	4.5	9	13.5	8
$Fraction\ remaining$	1	1/2	1/4	1/8	1/16

Answer: (c) 1/4 and 1/16 of the original.

Problem 35

Selenium-75 has a half-life of 120 days and is used medically for pancreas scans. (a) Approximately how much selenium-75 would remain of a 0.050 g sample that has been stored for one year? (b) How long would it take for a sample of selenium-75 to lose 99% of its radioactivity?

Solution

Solution to (a):

365 day / 120 day = 3.0417 half-lives

$(1/2)^{3.0417}$ = 0.12144 (this is the decimal amount that remains)

0.12144 x 0.050 g = 0.006072 g
to two sig figs = 0.0061 g

Solution to (b):

99% gone means 1% remaining, which is 0.01 as a decimal
$(1/2)^n = 0.01$
n log 0.5 = log 0.01
n = 6.643856 (this is the number of half-lives elapsed)
120 day times 6.643856 = 797 days

Problem 36
Natural samarium (average atomic mass 150.36) contains 14.99% of the radioactive isotope Sm-147. A 1 g sample of natural Sm has an activity of 89 decays per second. Estimate the half life of Sm-147.
Solution
1 g times 0.1499 = 0.1499 g of Sm-147
0.1499 g / 146.915 g/mol = 0.00102032 mol
0.00102032 mol times 6.022×10^{23} mol^{-1} = 6.144367×10^{20} atoms
6.144367×10^{22} atoms / 2 = 3.0721835×10^{20} atoms
3.0721835×10^{20} atoms / 89 decays/sec = 3.45189×10^{18} sec
3.45189×10^{18} sec = 1.094×10^{11} yr.

The Wiki article for isotopes of samarium gives 1.06×10^{11} yr.

Implicit in this solution is that the decays rate of 89 decays/second remains constant for the entire half-life. The decay rate actually becomes lesser over time but, for purposes of making an estimate, we ignore this.

Problem 37
You measure the radioactivity of a substance, then when measuring it 120 days later, you find that it only has 54.821% of the radioactivity it had when you first measured it. What is the half life of that substance? **Solution**
1) How many half-lives have elapsed in the 120 days?
$(1/2)^n = 0.54821$
n log 0.5 = log 0.54821
n = 0.8672
2) Determine the half-life.
120 day / 0.8672 = 138.4 day

Problem 38
Arsenic-74 is a medical radioisotopes with a half-life of 18 days. If the initial amount of arsenic-74 injected is 2.30 mCi, how much arsenic-74 is left in the body after 54 days?

Solution

54 days / 18 days = 3 half-lives elapsed

$(1/2)^3 = 0.125 \leftarrow$ amount remaining after three half-lives

2.30 mCi x 0.125 = 0.2875 mCi

to three sig figs, 0.288 mCi

Problem 39

Assume that today there is 10 grams of substance, while 1000 years ago there was 100 grams of it. If there is 15 grams of substance today, how much will there be 600 years from now?

Solution

1) What is needed is the length of the half-life.

10 g / 100 g = 0.1 $\leftarrow$ this is the decimal amount remaining after 1000 years

$(1/2)^n = 0.1 \leftarrow$ where n is the number of half-lives needed to elapse to give 0.1 remaining

n log 0.5 = log 0.1

n = 3.321928 half-lives

1000 yr / 3.321928 = 301.03 yr

2) Now, we turn to the 15 g sample. We need to know how many half-lives have elapsed

600 yr / 301.03 yr = 1.99316 half-lives

$(1/2)^{1.99316} = 0.251188 \leftarrow$ that's the decimal amount remaining after 600 years.

15 g is to 1 as x is to 0.251188

x = 3.8 g

Problem 40

A radionuclide, cobalt-60, has a half-life of 5.27 years. How many hours would it take for the activity to diminish to one-thirty-second (3.125%) of its original value?

Solution

$(1/2)^n = 0.03125$

n log 0.5 = log 0.03125

n = 5 (this is how many half-lives have elapsed)

5.27 x 5 = 26.35 years

You may convert years to hours.

Problem 41

Cf-249 is bombarded with an isotope of oxygen to produce Sg-263 and 4 neutrons. Write the full equation for this reaction.

Solution

1) Write what we know:

$$^{249}_{98}Cf + ^{??}O \rightarrow ^{263}_{106}Sg + 4^1_0n$$
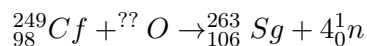
2) Determine the mass number:

249 + ?? = 263 + 1 + 1 + 1 + 1 (just emphasizing 4 neutrons)

?? = 18

3) Write the full equation:

$$^{249}_{98}Cf + ^{18}O \rightarrow ^{263}_{106}Sg + 4^1_0n$$

4) The short form:

$$^{249}_{98}Cf(^{18}O, 4^1_0n)^{263}_{106}Sg$$
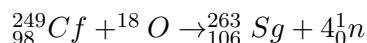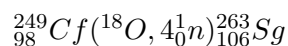
5) Some comments:

(a) the equation in this question is the discovery equation for element 106. It was discovered by a team led by Albert Ghiorso, the discoverer (or co-discoverer) of 12 elements, ranging from element 95 to element 106.

(b) "Nuclear Reactions and Synthesis of New Transuranium Species" is a survey written by Glenn Seaborg in 1983. Seaborg led the work in tranuranium elements, discovering plutonium in 1940 but not publishing his work until 1948 (due to WWII-related secrecy). Seaborg shared the 1951 Nobel Prize in Chemistry for this work.

(c)In response to a question, Seaborg stated that his personal opinion was that his doctoral advisor, Gilbert Newton Lewis, had committed suicide and not due to a laboratory accident. By the way, Seaborg was the one to find the body.

Problem 42

Convert 1 amu to MeV ?

Solution

1) Determine mass of 1 amu (in kg):

By definition, the mass of 1 atom of C-12 is 12 a.m.u

Therefore, the mass of one mole of C-12 atoms is, by definition, 12 g

Avogadro's Number is 6.0221409 x 10^{23} mol^{-1}

12 g/mol / 6.0221409 x 10^{23} mol^{-1}1 = 1.9926468 x 10^{-23} g (mass of one atom of C-12 in g)

(1.9926468 x 10^{-23} g) (1 kg / 1000 g) = 1.9926468 x 10^{-26} kg (mass of one atom of C-12 in kg)

1.9926468 x 10^{-26} kg/atom / 12 amu/atom = 1.660539 x 10^{-27} kg/amu (this

is the mass of 1 amu)

2) Use Einstein's mass-energy equation to determine Joules in one amu:
$E = mc^2$ E = (1.660539 x $^{-27}$ kg) (2.99792458 x 10^8 m/s)^2
E = 1.49242 x 10^{-10} kg-m^2/s^2 (this is Joules)

3) Convert J to eV, then MeV
1 eV = 1.60217733 x 10^{-19} J
1.49242 x 10^{-10} J / 1.60217733 x 10^{-19} J/eV = 931494893 eV
(931494893 eV) (1 MeV / 10^6 eV) = 931.494893 MeV
Often, 931.5 MeV is the value used in problem solving.

4) 931.5 MeV is the energy in one amu. Is it possible to express the mass
of one amu using MeV in some way? I'm glad you asked:
$E = mc^2$
931.5 MeV = mc^2
m = 931.5 MeV/c^2
The use of 931.5 MeV/c^2 for the mass of 1 u is wide-spread. So much so that
the c^2 is often not written and you must infer its presence by context.

5) To sum up:
1 u = 931.5 MeV (expressed as energy)
1 u = 931.5 MeV/c^2 (expressed as mass)
In solving problems, you may see this unit:
931.5 MeV/u-c^2
read it as 931.5 MeV/c^2 per 1 u

By the way, if you look around the Internet, you will find values different
than the 931.494893 value I calculated. This is because different authors will
use values that they have rounded off differently than the ones I used.

For example, I used 1.660539 x 10−27 kg for the mass of 1 amu. Often,
you will see it as 1.66 x 10^{-27} kg.

The cumulative effect of these rounding off decisions will be seen in
slightly different answers from different authors.

Problem 43
Calculate the energy released when the following fission reaction occurs:

$$^{235}_{92}U + ^1_0 n \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3^1_0 n + \gamma$$
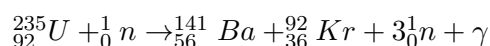
Discussion:

Some of the mass at the start (the U-235 and the neutron) will disappear during the fission. We have to subtract the total mass on the right-hand side from the total mass on the left-hand side. We will then use Einstein's mass-energy relation (E = mc^2) to calculate the energy generated in the fission. Report the value in MeV (megaelectron volts).

By the way, electrons are completely ignored. This is because the number of electrons remains constant on both sides of the reaction arrow.

Solution

1) Since the text of the example provides no data whatsoever, we must do some looking up. I have decided to start with the masses in unified atomic mass units:

Nuclide	Mass(u)	Nuclide	Mass(u)
$^{235}_{92}U$	235.04393	$^{141}_{56}Ba$	140.914411
$^{1}_{0}n$	1.008665	$^{92}_{36}Kr$	91.926156

2) Left-hand side:
235.04393 + 1.008665 = 236.052595 u

3) Right-hand side:
140.914411 + 91.926156 + (3)(1.008665) = 235.866562 u

4) The difference (known as the mass defect):
236.052595 - 235.866562 = 0.186033 u

From here, we can go a long way (steps 5 to 8) or a short way (step 9). It all depends on what you are given and what the teacher wants.
1 u = 1.6605402 x 10^{-27} kg

6) Convert u to kg:
(0.186033 u) (1.6605402 x 10^{-27} kg / u) = 3.08915275 x 10^{-28} kg

7) Use Einstein's mass-energy conversion:

$$E = mc^2$$

E = (3.08915275 x 10^{-28} kg) (2.99792458 x 10^8 m/s)^2
E = 2.7764 x 10^{-11} J
I used Joules because the unit kg-m^2/s^2 is the unit for Joules.

8) Last calculation is to convert J to MeV.
1 J = 6241506479963.2 MeV

$(2.7764 \times 10^{-11}\text{J})$ $(6241506479963.2 \text{ MeV / J}) = 173.3 \text{ MeV}$

9) This is the shorter way:
1 u = 931.494893 MeV / c^2
(0.186033 u) $(931.494893 \text{ MeV / u-}c^2) = 173.3 \text{ MeV}/c^2$

Problem 44

Calculate the energy (in both J and MeV) released in the fusion reaction between deuterium and tritium. The reaction produces helium-4 and a neutron.

Solution

1) The first thing to do is write the reaction

$$^3_1H +^3_1 H \to^4_2 He +^1_0 n + Q$$
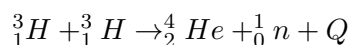
2) Secondly, we need the atomic masses of each nuclide:
Deuterium 2.014101778 u
Tritium 3.016049282 u
Helium-4 4.002603254 u
neutron 1.008664916 u

3) Add the two reactants and the two products, then compute the difference:
(2.014101778 + 3.016049282) - (4.002603254 + 1.008664916)
5.03015106 - 5.01126817
0.01888289 u ←this is known as the mass defect

3) Next, we need to convert the mass defect (in atomic mass units) to kilograms. The conversion factor is 1 u = 1.6605402 x 10^{-27} kg.
(0.01888289 u) $(1.6605402 \times 10^{-27} \text{ kg/u}) = 3.1355798 \times 10^{-29}$ kg

4) Use Einstein's famous formula to calculate the energy:
E = mc^2
E = $(3.1355798 \times 10^{-29} \text{ kg})$ $(299792458 \text{ m/s})^2$
E = $2.8181186 \times 10^{-12}$ J

5) To determine the answer in MeV (megaelectron volt), we use the conversion factor of 1 J = 6.24150648 x 10^{12} MeV.
$(2.8181186 \times 10^{-12} \text{ J})$ $(6.24150648 \times 10^{12} \text{ MeV / J}) = 17.589$ MeV

6) The kJ/mol has been used for the energy amount. My value of 17.589 MeV is for the reaction of one nuclide of H-2 with one nuclide of H-3 whereas his is for a mole of nuclides. The author does a fission example as well.

3.4.1 Half-life problems involving carbon-14

Problem 01

A chemist determines that a sample of petrified wood has a carbon-14 decay rate of 6.00 counts per minute per gram. What is the age of the piece of wood in years? The decay rate of carbon-14 in fresh wood today is 13.6 counts per minute per gram, and the half life of carbon-14 is 5730 years.

Solution

1) Determine decimal fraction of C-14 remaining:

6.00 / 13.6 = 0.4411765

2) Determine how many half-lives have elapsed:

$(1/2)^n = 0.4411765$

n log 0.5 = log 0.4411765

n = 1.18057

3) Determine length of time elapsed:

5730 yr x 1.18057 = 6765 yr

Problem 02

The carbon-14 decay rate of a sample obtained from a young tree is 0.296 disintegration per second per gram of the sample. Another wood sample prepared from an object recovered at an archaeological excavation gives a decay rate of 0.109 disintegration per second per gram of the sample. What is the age of the object?

Solution

1) Determine decimal fraction of C-14 remaining:

0.109 / 0.296 = 0.368243

2) Determine how many half-lives have elapsed:

$(1/2)^n = 0.368243$

n log 0.5 = log 0.368243

n = 1.441269

3) Determine length of time elapsed:

5730 yr x 1.441269 = 8258 yr

Problem 03

The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees (indicating 70% of the C-14 had decayed). How old is that piece of wood?

Solution

1) Determine decimal fraction of C-14 remaining:

0.300 (from text of problem)

2) Determine how many half-lives have elapsed:

$(1/2)^n = 0.300$

n log 0.5 = log 0.300

n = 1.737

3) Determine length of time elapsed:

5730 yr x 1.737 = 9953 yr

Problem 04

Carbon-14 is used to determine the age of ancient objects. If a sample today contains 0.060 mg of carbon-14, how much carbon-14 must have been present in the sample 11,430 years ago?

Solution

1) Determine half-lives elapsed:

11,430 / 5730 = 1.9947644

2) Determine decimal fraction remaining:

$(1/2)^{1.9947644}$ = x

x = 0.25091

3) Use a ratio and proportion to find C-14 present in the past:

(0.060 mg / 0.25091) = (x / 1)

x = 0.239 mg

Problem 05

All current plants have a C-14 count of 15.3 cpm. How old is a wooden artifact if it has a count of 9.58 cpm?

Solution

1) Determine decmal fraction remaining:

9.58 / 15.3 = 0.6261438

2) Determine half-lives elapsed:

$(1/2)^n$ = 0.6261438

n log 0.5 = log 0.6261438

n = 0.675434

3) Determine number of years:

5730 years x 0.675434 = 3870 years

Problem 06

Using dendrochronology (using tree rings to determine age), tree materials dating back 10,000 years have been identified. Assuming you had a sample of such a tree in which the number of C-14 decay events was 15.3 decays per minute before decomposition, what would the decays per minute be in the present day?

Solution

10,000 yr / 5730 yr = 1.7452 half-lives

$(1/2)^{1.7452}$ = 0.2983 (this is the decimal amount remaining)

15.3 times 0.2983 = 4.56 (rounded off to three sig figs)

Problem 07

A mammoth skeleton has a carbon-14 decay rate of 0.0077 disintegrations per second per gram of carbon. How long ago did the mammoth live? (Assume that living organisms have a carbon-14 decay rate of 0.255 s^{-1} g^{-1} and that carbon-14 has a half-life of 5730 y.)

Solution

0.0077 / 0.255 = 0.030196

$(1/2)^n$ = 0.030196

n log 0.5 = 0.030196

n = 5.0495

(5730 y) (5.0495) = 28933.635 y

29000 y seems a reasonable answer to report

Comment: the skeleton itself was not dated by C-14 since no organic material remains in the bones. However, organic material the skeleton was buried in was dated or perhaps food in its stomach was dated (which has happened).

Problem 08

All living things have a steady state C-14 activity of 15.3 atoms min^{-1} g^{-1}. Suppose a sample of cloth from an archeological site shows an activity of 0.372 atoms min^{-1} g^{-1}. How old is the cloth?

Solution

0.372 / 15.3 = 0.0243137 (this is the decimal amount of activity remaining)

$(1/2)^n = 0.0243137$

n log 0.5 = log 0.0243137

n = 5.362 (this is how many half-lies have passed)

(5730 yr) (5.362(= 30724.26 yr

Problem 09

The smallest C-14 activity that can be measured is about 0.20%. If C-14 is used to date an object, the object must have died within how many years?

Solution

In decimal form, 0.20% is 0.0020. This is the amount remaining.

$(1/2)^n = 0.0020$

n log 0.5 = log 0.0020

n = 8.9658 ← this is how many half-lives have elapsed

(5730 yr) (8.9658) = 51374 yr

Problem 10

How long will it take for 25% of the C-14 atoms in a sample of C-14 to decay?

Solution

25% decay means 75% remains

$(1/2)^n = 0.75$

n log 0.5 = log 0.75

n = 0.415

(5730 yr) (0.415) = 2378 yr

Chapter 4

Electronic Structure of the Atom

4.1 Important Concepts and Course Review

♣ **The Electron Shell**
♠ **Wave-Particle Duality of Light (Einstein 1905)**
All electromagnetic radiation exhibits **dual periodicity**:
- **Spatial**, defined by the wavelength λ (in meters) or its inverse, the wavenumber σ (in m^{-1});
- **Temporal**, characterized by the period T (in seconds) or its inverse, the frequency ν (in Hz).
These two periodicities are related by:

$$\lambda = \frac{1}{\sigma} = CT = \frac{C}{\nu}$$

where C = 3×10^8 m/s, the speed of light in a vacuum.

Any monochromatic radiation with frequency ν can also be described as a **stream of massless particles**. These particles are called **photons**, and each carries energy E = h $\times$ ν (in J).
h = 6.63×10^{-34} J·s is the **Planck constant**.

♠ **Light-Matter Interaction**
Any atom with energy E_1 can reach an energy state $E_2 > E_1$ by **absorbing a photon** with energy hν. This transition from one energy state to another is also called a **transition**. Conversely, any atom with energy E_2 can de-excite to an energy state $E_1 < E_2$ by **emitting a photon** with energy hν, conserving the total energy of the system (atom + photon): $\boxed{E_2 = E_1 + h\nu}$
The line spectra obtained in atomic spectroscopy, either in absorption or emission, reflect the discontinuous nature of energy exchange between electromagnetic radiation and matter. These exchanges occur in energy quanta E = hν.

Analyzing the distribution of lines in a spectrum, identified by their wavenumber $\bar{\nu} = 1/\lambda$, has led to grouping the lines into **spectral series**.
For the hydrogen emission spectrum, the following empirical formula resulted from the work of **Balmer** and **Ritz**:

$$\bar{\nu} = R_H \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

where: $R_H = 1.0967558 \times 10^7$ m^{-1} is the **experimental Rydberg constant**. n and n' are two integers such that $n \geq 1$ and $n' > n$. Each spectral series consists of lines. The distinct series include **Lyman** ($n = 1$, UV emission), **Balmer** ($n = 2$, mainly in the visible), **Paschen** ($n = 3$, IR), **Brackett** ($n = 4$, IR), **Pfund** ($n = 5$, IR).

♠ **Energy Quantization of the Atom and Bohr Model**
The energy of the atom is quantized and can only take certain values based on the **principal quantum number** n, an integer ≥ 1. The successive values $n = 1$, 2, 3, etc., define energy levels or shells. The atom's ground state is its lowest energy state.

In Bohr's model, electrons (assumed to be point-like particles with mass m) move in uniform circular orbits around the nucleus. It postulates that, for these orbits to be stable, the electron's velocity V and the radius r of its orbit must be related by:
mvr = n $\dfrac{h}{2\pi}$ = nh, where n is a **non-zero integer**, and h is the Planck constant.
In the context of the Bohr model, the possible electron orbits have radii r = $n^2 a_0$, and the corresponding total energy of the hydrogen atom is $E_n = -\dfrac{E_0}{n^2}$.
where $a_0 = 0.53$ Å is the Bohr radius and $E_0 = 13.6$ eV $= 2.18 \times 10^{-18}$ J.
Emission lines correspond to transitions from a higher energy level of the atom to a lower one: $n' \to n$. The corresponding energy loss is de-excitation.
Absorption lines correspond to excitation: $n \to n'$.

4.2 Exercise Statements

Exercise 01

When a light radiation with a wavelength of 350 nm strikes a sodium (Na) metal surface, electrons are emitted with kinetic energy equal to 1.3 eV.

  - Calculate the initial frequency of sodium.

- Calculate the work required to extract one mole of electrons from sodium.

Exercise 02

A cesium photoelectric cell is successively illuminated by two radiations with frequencies $\nu_1 = 42857 \times 10^{10}$ s^{-1} and $\nu_2 = 55556 \times 10^{10}$ s^{-1}. The energy required to extract an electron from this metal is $E_0 = 3 \times 10^{-19}$ J.

- Calculate the threshold frequency ν_0.

- Under what conditions does the photoelectric effect occur?

- In the case of the photoelectric effect, calculate the maximum velocity of the electrons ejected from the metal.

Data: $c = 3 \times 10^8$ m/s; $h = 6.62 \times 10^{-34}$ J.s; m= 9.1×10^{-31} Kg; $e = 1.6 \times 10^{-19}$ C.

Exercise 03

In the emission spectrum of hydrogen, two cases are represented in the following figure:
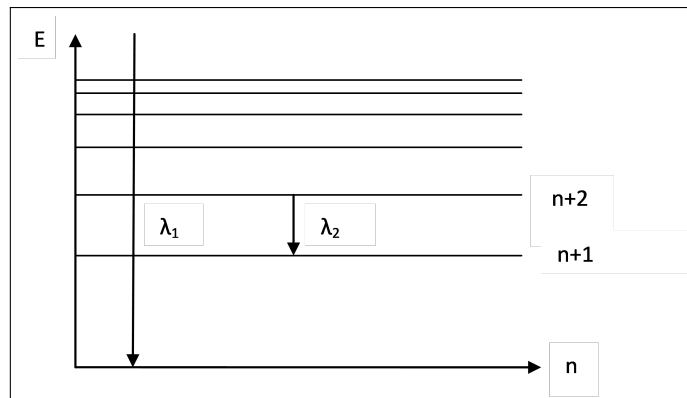
Figure 4.1: Hydrogen emission spectrum

The wavelength of the limit line is 820.8 nm.

1. Calculate n.

2. Which series does it belong to?

3. Calculate the value of λ_2.

Data: $R_H = 1.09700 \times 10^7$ m^{-1}; $h = 6.62 \times 10^{-34}$ J.s; c $= 3 \times 10^8$ m/s.

Exercise 04

I. According to Bohr's theory, there are only a certain number of possible electron energy levels in the hydrogen atom.

1. Calculate in eV the energies corresponding to the first 4 levels and represent them schematically on a scale (maintaining the scale).

2. Calculate the radii of these orbits.

3. What is the minimum amount of energy that an hydrogen atom must absorb to transition from the ground state to the excited state? If this energy is provided in the form of light, what is the wavelength of the required radiation?

II. An hydrogen atom in its ground state absorbs a photon with a wavelength $\lambda = 974$ Å . What is the energy level of the electron after absorption?
III. Consider the hydrogen-like ion He$^+$, and the transition from $n_1 = 1$ to $n_2 = 2$ results in a wavelength of 30.3 nm.

1. Calculate R_{He^+}, deduce a relationship between R_H and R_{He^+}, as well as the atomic number of He^+.

2. Calculate the energy of the fundamental level of the He^+ ion in Joules and eV.

3. Calculate the ionization energy of the hydrogen-like ion from its ground state.

Exercise 05

Consider a hydrogen atom in an excited state (n=4). Among all the paths that allow it to return to its ground state, we consider 2 cases:
- one accompanied by the emission of a single photon with frequency ν_1;
- one accompanied by the emission of 3 photons (frequencies ν_2, ν_3, and ν_4 successively).
a- Deduce the transitions that occur in both cases, specifying the values of the corresponding wavelengths λ_1, λ_2, λ_3, and λ_4.

b- Is there a relationship between ν_1 and the sum $(\nu_2 + \nu_3 + \nu_4)$? If yes, explain what it is. <u>Given</u>: $R_H = 109677$ cm^{-1}.

Exercise 06

The energy of a hydrogen atom can be expressed as:

$E_n = E_H$ (E_H = -13.6 eV = energy of the ground state of the hydrogen atom).

Consider the hydrogen atom and the hydrogen-like ion U^{91+} (U = uranium).

1- Establish the relationship between the ionization energies of these two hydrogenoids and calculate them. Was this result predictable?

2- Establish, as a function of Z (nuclear charge) and E_H, the expression for the wavelength of the radiation that can cause a transition from the ground state to the first excited state. Calculate for hydrogen and the hydrogen-like ion U^{91+} and compare the results obtained.

<u>Data</u>: 1 eV = 1.6 $\times 10^{-19}$; c = 3 $\times 10^8$ m/s; h = 6.6 $\times 10^{-34}$.

Exercise 07

a. In a Balmer series of the hydrogen atom, the frequency of the line corresponding to the shortest wavelength is: $\nu = 8.227 \times 10^{14}$ s^{-1}. Calculate the Rydberg constant.

b. A light radiation with a wavelength $\lambda = 0.1 \times 10^{-9}$m causes the ionization of a hydrogen-like atom from its ground state.

    1. Calculate the atomic number Z and the ionization energy of this atom.

    2. Calculate the electron's orbit radius for this atom, which is in the first excited state, using the Bohr model.

    <u>Data</u>: Bohr radius: $a_0 = 0.53$ Å; Planck's constant: $h = 6.62 \times 10^{-34}$J.s

Exercise 08

The values of excitation energy for the hydrogen atom are: 12.99; 12.69; 12.03; 10.15 eV. The value of ionization energy is 13.54 eV. Express the energy values of the electron at different levels in eV, and deduce that these experimental results confirm Bohr's theory.

Exercise 09

The study of the photosynthesis of green plants shows that eight quanta of red light ($\lambda = 685$ nm) are required to release a molecule of dioxygen due to the oxidation of water. After briefly recalling what photosynthesis consists of, calculate the energy efficiency of this oxidation, knowing that the electrical work required for the photooxidation is 470 kJ/mol.

4.3   Exercise Solutions

Exercise 01

a) The total energy resulting from the photoelectric effect is equal to the sum of the initial energy (when the radiation hits the metal) and the kinetic energy of the emitted electrons.

Let: $E = E_0 + E_c$ $h\nu = h\nu_0 + E_c \Rightarrow \nu_0 = \dfrac{h\nu - E_c}{h} = \dfrac{h\left(\dfrac{c}{\lambda}\right) - E_c}{h}$

$\nu_0 = \dfrac{c}{\lambda} - \dfrac{E_c}{h} = \dfrac{3 \times 10^8}{350 \times 10^{-9}} - \dfrac{1.3 \times 1.6 \times 10^{-19}}{6.62 \times 10^{-34}} \Rightarrow \boxed{\nu_0 = 5.43 \times 10^{14} s^{-1}}$

b) The work required to extract 1 mole of electrons is: $W = \mathcal{N} h\nu_0$
$\Rightarrow W = 6.023 \times 10^{23} \times 6.62 \times 10^{-34} \times 5.43 \times 10^{14} \Rightarrow \boxed{W = 2.16 \times 10^5 \text{ Joules}}$

Exercise 02

1) The photoelectric effect occurs only if $\nu \geq \nu_0$, where ν_0 is the threshold frequency. $\nu_0 = \dfrac{E_0}{h} = \dfrac{3 \times 10^{-19}}{6.63 \times 10^{-34}} \Rightarrow \boxed{\nu_0 = 45317 \times 10^{10} \text{ s}^{-1}}$

2) In the case of the photoelectric effect: $\nu_1 > \nu_0 > \nu_2$
- When $\nu_1 < \nu_0$, there is no photoelectric effect.
- When $\nu_2 > \nu_0$, there is a photoelectric effect.

3) Calculation of the speed of electrons: $E_c = h\nu - h\nu_0$
$\frac{1}{2}mv^2 = h\nu_2 - E_0$
$v^2 = \dfrac{2(h\nu_2 - E_0)}{m}$
$v^2 = \dfrac{2[(6.63 \times 10^{-34} \times 55556 \times 10^{10}) - 3 \times 10^{-19}]}{9.1 \times 10^{-31}} \Rightarrow \boxed{\text{Speed} = 3.873 \times 10^5 \text{ m/s}}$

Exercise 03

1) Transition:
$n = \infty \xrightarrow{\lambda_1} n$
$n + 2 \xrightarrow{\lambda_2} n + 1$
$\lambda_1 = 820.8 \, nm \Rightarrow \lambda_1 = 820.8 \times 10^{-9} m$
$\dfrac{1}{\lambda_1} = R_H \left(\dfrac{1}{n^2} - 0\right) \Rightarrow \dfrac{1}{\lambda_1} = \dfrac{R_H}{n^2}$
$\Rightarrow n^2 = \lambda_1 \times R_H \Rightarrow n^2 = 820.8 \times 10^{-9} \times 1.09 \times 10^7 = 9 \Rightarrow \boxed{n = 3}$ (Paschen series)

2) Calculation of λ_2:

When $n = 3 \Rightarrow \begin{cases} n + 2 \longrightarrow 5 \\ n + 1 \xrightarrow{\lambda_2} 4 \end{cases}$

$\dfrac{1}{\lambda_2} = R_H \times \left(\dfrac{1}{4^2} - \dfrac{1}{5^2}\right) \Rightarrow \dfrac{1}{\lambda_2} = 0.025 \times 10^7 m^{-1} \Rightarrow \boxed{\lambda_2 = 4 \times 10^{-6} \text{ m}}$

Exercise 04

I. 1) We have $E_n = \dfrac{Z^2}{n^2} \times E_1$ with $E_1 = -13.6\ eV$.

When $Z = 1$, $n = 1 \Rightarrow E_1 = -13.6\ eV$.

The energies for the first four energy levels are: $E_1(n = 1)$, $E_2(n = 2)$, $E_3(n = 3)$, and $E_4(n = 4)$

$$\begin{cases} n = 2 \Rightarrow E_2 = \left(\dfrac{1}{4}\right) \times 13.6 = -3.40\ eV \\[2mm] n = 3 \Rightarrow E_3 = \left(\dfrac{1}{9}\right) \times 13.6 = -1.51\ eV \\[2mm] n = 4 \Rightarrow E_4 = \left(\dfrac{1}{16}\right) \times 13.6 = -0.85\ eV \end{cases}$$
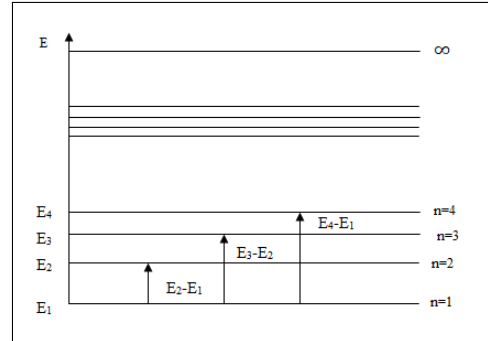
Figure 4.2: Schematic representation of energy levels

2) Calculation of the radii of the orbits. $n = 1 \Rightarrow r_1 = \dfrac{n^2}{Z} \cdot r_1$

$$r_1 = 0.53 \times 10^{-10}\ \text{m} = 0.53\ \text{Å} \begin{cases} n = 2 \Rightarrow r_2 = \left(\dfrac{4}{1}\right) \times (0.53\ \text{Å}) = 2.12\ \text{Å} \\[2mm] n = 3 \Rightarrow r_3 = \left(\dfrac{3^2}{1}\right) \times (0.53\ \text{Å}) = 4.77\ \text{Å} \\[2mm] n = 4 \Rightarrow r_4 = \left(\dfrac{4^2}{1}\right) \times (0.53\ \text{Å}) = 8.48\ \text{Å} \end{cases}$$

3) It is clear that $(E_4 - E_1) > (E_3 - E_1) > (E_2 - E_1)$

$\Rightarrow$ The smallest absorbed energy is $\Delta E = E_2 - E_1 = 10.21$ eV

Wavelength

$$\Delta E = 10.21\ \text{eV} \Rightarrow \Delta E = \dfrac{h \cdot c}{\lambda}\ (\Delta E = h{\cdot}\nu)\ \lambda = \dfrac{h \cdot \nu}{\Delta E} = \dfrac{6.63 \times 10^{-34} \cdot 3 \times 10^8}{10.21 \times 1.6 \times 10^{-19}}$$

$\Rightarrow \boxed{\lambda = 1.2 \times 10^{-7}\ \text{m}}$

II. Transition

$n_1 = 1 \overset{\lambda}{\to} n_2$

$\lambda = 974.00 \times 10^{-12}$ m

$\Rightarrow \dfrac{1}{\lambda} = R_H \left(\dfrac{1}{(n_1)^2} - \dfrac{1}{(n_2)^2} \right)$

$\Rightarrow \dfrac{1}{\lambda . R_H} = 1 - \dfrac{1}{(n_2)^2}$

$\Rightarrow n_2 = \sqrt{\dfrac{1}{1 - \dfrac{1}{\lambda . R_H}}}$

$$\Rightarrow n_2 = \sqrt{\dfrac{1}{1 - \dfrac{1}{974 \times 10^{-10} \times 1.09786 \times 10^7}}}$$

$$\Rightarrow \boxed{n_2 = 4}$$

III.

1) $He^+ : n_1 = 1 \rightarrow n_2 = 2$

$$\Rightarrow \frac{1}{\lambda_{He^+}} = R_{He^+} \left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2} \right)$$

$$\Rightarrow R_{He^+} = \frac{1}{30.3 \times 10^{-9} \times \left(1 - \dfrac{1}{4} \right)}$$

$$\Rightarrow \boxed{R_{He^+} \approx 4.4 \times 10^7 m^{-1}}$$

We have $\begin{cases} \dfrac{1}{\lambda R_{He^+}} = R_{He^+} \left(\dfrac{1}{(n_1)^2} - \dfrac{1}{(n_2)^2} \right) \\ \dfrac{1}{\lambda_{He^+}} = (Z_{He^+})^2 \times R_H \left(\dfrac{1}{(n_1)^2} - \dfrac{1}{(n_2)^2} \right) \end{cases}$

$$\Rightarrow R_{He^+} = (Z_{He^+})^2 \times R_H \Rightarrow (Z_{He^+})^2 = \frac{R_{He^+}}{R_H} = \frac{4.4 \times 10^7}{1.1 \times 10^7} = 4$$

$$\Rightarrow \boxed{Z_{He^+} = 2}$$

2) Ground state energy:

$$n_1 = 1 \rightarrow E_1(He^+) = \frac{(Z_{He^+})^2}{(n_1)^2} \times E_1(H)$$

$$E_1(He^+) = \frac{2^2}{1} \times (-13.6 \ eV) \Rightarrow \boxed{E_1(He^+) = -54.4 \ eV}$$

$$\Rightarrow \boxed{E_1(He^+) = -90.30 \times 10^{-19} \text{ joules}}$$

4) Ionization energy:

$E_i(He^+) = E_\infty - E_1(He^+)$

$\Rightarrow E_i(He^+) = -E_1(He^+) = 54.4 \ eV$

Exercise 05

a- In the first case, it is a transition from 4 to 1. In the second case, it involves the successive transitions 4-3, 3-2, 2-1 (these integers correspond to the principal quantum numbers characterizing the different energy levels).

We determine the wavelengths using: $\dfrac{1}{\lambda} = R_H \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$

Numerical application:
1 = 4-1 = 97.26 nm
2 = 4-3 = 18.75 nm
3 = 3-2 = 656.4 nm
4 = 2-1 = 121.57 nm.

b- By directly writing the energy differences of the considered levels, we have:

$$E_4 - E_1 = (E_4 - E_3) + (E_3 - E_2) + (E_2 - E_1)$$

So: $h\nu_1 = h\nu_2 + h\nu_3 + h\nu_4$

This explains the simple relationship between the frequencies: $\nu_1 = \nu_2 + \nu_3 + \nu_4$

Exercise 06

1- $E_{n_{(U+91)}} = (Z^2/n^2)E_H$ (E_H = -13.6 eV)

$E_{I_{(U+91)}} = Z^2 \times E_{I_{(H)}}$

$$\Rightarrow \begin{cases} E_{I_{(H)}} = 13.6 eV \\ E_{I_{(U+91)}} = 1.15 \times 10^5 eV \end{cases}$$

These results are predictable because $Z \uparrow E_{I_{(Hydrogenoid)}} \uparrow$.

2- $\Delta E = E_2 - E_1 = (3/4) Z^2 E_H = \dfrac{h}{\lambda c}$

$$\Rightarrow \boxed{\lambda = \frac{1}{Z^2} \times \frac{hc}{-(3/4)E_H}}$$

$$\Rightarrow \begin{array}{l} H \rightarrow \lambda = 1210 \ \mathring{A} \\ U \rightarrow \lambda = 0.14 \ \mathring{A} \end{array}$$

$$\lambda_H \longrightarrow UV$$
$$\lambda_U \longrightarrow X - ray$$

Exercise 07

a. Calculation of the constant R_H:

According to the Balmer equation, the wavelength of a light radiation is given by:

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right)$$

The smallest wavelength corresponds to the highest energy value, i.e., at the limit $n_2 = \infty$ and $n_1 = 2$

which yields $\dfrac{1}{\lambda} = \dfrac{R_H}{4} \Rightarrow R_H = \dfrac{4}{\lambda} = \dfrac{4\nu}{C} = \dfrac{4 \times 8.227 \times 10^{14}}{3 \times 10^8}$

$$\Rightarrow \boxed{R_H = 1.096 \times 10^7 \ m^{-1}}$$

b.

1. Ionization from the ground state:

$n_1 = 2, n_2 = \infty$

$$\frac{1}{\lambda} = \frac{Z^2}{4} \times R_H$$

$$\Rightarrow Z = \sqrt{\frac{4}{\lambda \times R_H}} = \sqrt{\frac{4}{0.1 \times 10^{-9} \times 1.096 \times 10^7}}$$

$$\Rightarrow \boxed{Z = 2}$$

Ionization energy

$E_i = h\nu$

$$E_i = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{0.1 \times 10^{-9}} = 19.86 \times 10^{-16} J$$

2. First excitation: n=2

$$r = a_0 \frac{n^2}{Z} = 0.53 \times \frac{4}{2}$$

$$\Rightarrow \boxed{r = 1.06 \text{ Å}}$$

Exercise 08

We are given the energy variations between consecutive levels $\Delta E_{n \to n+1}$ as follows:

$$\Delta E_{1 \to 2} = 10.15 = W_L - W_K$$
$$W_L = 10.15 + W_I$$
$$W_L = 10.15 - 13.34$$
$$\Rightarrow \boxed{W_L = -3.39 \ eV}$$

Similarly, we obtain:

$$\boxed{W_M = -1.51 \ eV} \qquad \boxed{W_N = -0.85 \ eV} \qquad \boxed{W_0 = -0.55 \ eV}$$

Verification of these results according to Bohr's theory: the total energy of an electron in a level of rank n is:

$$W = \frac{W_K}{n^2}$$

n=2; $W_L = -\dfrac{13.54}{4} = -3.385 \ eV$

$$n = 3; W_M = -1.50 \ eV$$
$$n = 4; W_N = -0.85 \ eV$$
$$n = 5; W_0 = -0.54 \ eV$$

The experimental results confirm Bohr's theory.

Exercise 09

During plant photosynthesis, carbon dioxide is reduced to glucose, and water is oxidized to dioxygen O_2. This occurs in the chloroplasts of green leaves when exposed to light. This transformation is the opposite of glucose combustion.

Photosynthesis, like all photochemical processes, is not thermodynamically favorable (free enthalpy of reaction: $\Delta_r G > 0$) and draws the required energy for its progress from absorbed light energy.

The energy of a quantum of light with wavelength λ is:

$$E = \frac{h \times c}{\lambda}$$

– The electrical work required for the production of one molecule of dioxygen by water oxidation according to:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
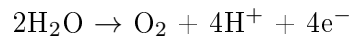
is $W/\mathcal{N}$ (on the elementary scale, $\mathcal{N}$ being Avogadro's constant).

– The absorbed energy is that of eight quanta, i.e., $8 \times E$.

– The energy efficiency (denoted by Rdt) is the fraction of the provided light energy actually used by the oxidation reaction, i.e.:

$$\text{Rdt} = \frac{W/\mathcal{N}}{8 \times E} = \frac{\lambda \times W}{8 \times h \times C \times \mathcal{N}}$$

Note. Efficiency is expressed as the ratio of a quantity's value (energy, mass, amount of substance, etc.) to its maximum value, and it is used to compare the two values. Efficiency has no unit and is between 0 and 1. It is customary to multiply it by 100 to express it as a percentage.

4.4 Problems

Problem 01

What is the frequency of electromagnetic radiation having a wavelength of 210.0 nm?

Solution

1) Convert nm to m:

210.0 nm x (1 m / 10^9 nm) = 210.0 x 10^{-9} m

We can leave it right there or convert it to scientific notation:

2.100 x 10^{-7} m

Either way works fine in the following calculation. Check with your teacher to see if they have a preference. Then, follow their preference.

2) Use $\lambda\nu = c$

(2.100 x 10^{-7} m) (ν) = 3.00 x 10^8 m/s

ν= 3.00 x 10^8 m/s divided by 2.100 x 10^{-7} m

ν= 1.428 x 10^{15} s^{-1}

Problem 02

What is the frequency of violet light having a wavelength of 4000 Å ?

Solution

The solution below depends on converting Å into cm. This means you must remember that the conversion is 1 Å = 10^{-8} cm. The solution:

$\lambda\nu = c$

(4000 x 10^{-8} cm) (ν) = 3.00 x 10^{10} cm/s ← note use of cm/s rather than m/s

ν = 7.50 x 10^{14} s^{-1}

Notice how I did not bother to convert 4000 x 10^{-8} into scientific notation. If I had done so, the value would have been 4.000 x 10^{-5}. Note also that I effectively consider 4000 to be 4 significant figures.

<u>Comment</u>: be aware that the range of 4000 to 7000 Å is taken to be the range of visible light. Notice how the frequencies stay within more-or-less the middle area of 10^{14}, ranging from 4.29 to 7.50, but always being 10^{14}. If you are faced with this calculation and you know the wavelength is a visible one (say 5550 Å, which is also 555 nm), then you know the exponent on the frequency MUST be 10^{14}. If it isn't, then YOU (not the teacher) have made a mistake.

Problem 03

What is the frequency of EMR having a wavelength of 555 nm? (EMR is an abbreviation for electromagnetic radiation.)

Solution

1) Let us convert nm into meters. Since one meter contains 10^9 nm, we have the following conversion:

555 nm x (1 m / 10^9 nm)

555 x 10^{-9} m = 5.55 x 10^{-7} m

2) Inserting into $\lambda\nu = c$, gives:

$(5.55 \times 10^{-7}$ m$)$ (x) $= 3.00 \times 10^8$ m s^{-1}

x $= 5.40 \times 10^{14}$ s^{-1}

Problem 04

What is the wavelength (in both cm and Å) of light with a frequency of 6.75 x 10^{14} Hz?

Solution

The fact that cm is asked for in the problem allows us to use the cm/s value for the speed of light:

(x) $(6.75 \times 10^{14}$ s$^{-1}) = 3.00 \times 10^{10}$ cm s^{-1}

x $= 4.44 \times 10^{-5}$ cm

Next, we convert to Å:

$(4.44 \times 10^{-5}$ cm$)$ x $(10^8$ Å / 1 cm$) = 4440$ Å

I could also have used (1 Å / 10^8 cm) for the conversion. I have a practice of putting the one with the larger unit (the cm in this case) and then figuring out how many of the smaller unit (the Å) there are in one of the larger unit.

Problem 05

Which of the following represents the shortest wavelength?

(a) 6.3×10^{-5} cm

(b) 7350 nm

(c) 3.5×10^{-6} m

Solution

1) Convert the wavelengths such that they are all the same unit. I choose to convert to nanometers and will start with (a):

$(6.3 \times 10^{-5}$ cm$)$ $(10^9$ nm / 10^2 cm$) = 630$ nm

One immediate conclusion is that (b) is not the correct answer.

2) The conversion for (c)

$(3.5 \times 10^{-6}$ m$)$ $(10^{99}$ nm / 1 m$) = 3600$ nm

(a) is the correct answer.

Problem 06

(a) Identify $\lambda\nu = c$ as either a direct or inverse mathematical relationship.

(b) Do the same for E = hν.

(c) Write a mathematical equation for the relationship between energy and wavelength.

(d) Identify the equation for (c) as either direct or inverse.

Solution

(a) $\lambda\nu = c$ is an inverse relationship. As one value (say the wavelength) goes up, the other value (the frequency) must go down. Why? Because the product of the two must always equal the same value, c, which is a constant.

(b) E = $h\nu$ is a direct relationship. As the frequency increases, so does E. Why? Because h remains constant. Notice that in this equation the two quantities which can change (ν and E) are on DIFFERENT sides of the equation whereas in the inverse relationship in (a), both λ and ν are on the same side, with the constant on the opposite side.

(c) Rearrange the light equation thusly:

$\nu = c/\lambda$

Substitute for ν in E = hν:

E = hc / λ ← use this equation when asked to calculate E after being given the wavelength.

Rearrange to group the variables and the constants:

Eλ = hc

(d) The mathematical relationship is an inverse one. Note the equation's similarity to $\lambda\nu$ = c, with two values that can vary on the left side and a constant (h times c) on the right.

Problem 07

How many Joules of energy are contained in a photon with λ = 550 nm? How many kJ/mol of energy is this?

Solution

1) Use $\nu = c/\lambda$ to get the frequency:

ν = (3.00 x 10^8 m s^{-1}) / (550 x 10^{-9} m)

ν= 5.4545 x 10^{14} s^{-1}.

I left a couple guard digits in the answer. Also, notice that the wavelength is not in scientific notation. This is because I made a silent conversion from nm to m. I didn't bother to convert it because it wasn't needed. be careful, your teacher may want you to have all numbers in scientific notation.

2) Now use E = hν to get the energy:

E = (6.626 x 10^{-34} J s) (5.4545 x 10^{14} s^{-1})

E = 3.614 x 10^{-19} J

This is the energy for one photon.

3) The last step is to find the kilojoules for one mole and for this we use Avogadro's Number:

Dividing the answer by 1000 to make the change to kilojoules, we get 217.6 kJ/mol

A slightly different way would be to use Eλ = hc (with the wavelength in meters) and solve for E, then multiply the answer times Avogadro's Number. Finally, divide by 1000 to get kJ/mol.

Problem 08

How many kJ/mol (remember: mol means mole of photons) of energy is contained in light with a wavelength of 496.36 nm?

Solution

1) Convert 496.36 nm to meters:

496.36 nm times (1 m / 10^9 nm) = 496.36 x 10^{-9} m

2) Use Eλ = hc

(E) (496.36 x 10^{-9} m) = (6.626 x 10^{-34} J s) (3.00 x 108 m s^{-1})

E = 4.0048 x 10^{-19} J

3) Multiply by Avogadro's Number:

4.0048 x 10^{-19} J times 6.022 x 10^{23} mol^{-1} = 241166 J/mol

241 kJ/mol (to three sig figs)

Problem 09

What is the energy of a photon of green light with a frequency of 5.76 x 10^{14} s^{-1}.

Solution

x = (6.626 x 10^{-34} J s) (5.76 x 10^{14} s^{-1})

x = 3.82 x 10^{-19} J

Comment: all frequencies of visible light will have an energy in the 10^{-19} J range of values. If you wish to, you may calculate this for yourself. The wavelength range of visible light is taken to be from 400 nm to 700 nm. This translates (more-or-less) to a range from 5 x 10^{-19} J down to 3 x 10^{-19} J

Problem 10

When excited, some atoms produce an emssion with a frequency of 7.25 x 10^{12} Hz.

(a) calculate the energy, in Joules, for one photon with this frequency.

(b) calculate the energy, in kJ/mol.

(c) Is this light visible? Why or why not?

Solution

Comments on the solution:

(a) use E = hν

(b) use Avogadro's number as well as the answer from (a). Make sure to convert from the J value (which is what you'll calculate) to the kJ value.

(c) Calculate the wavelength using $\lambda\nu$ = c. What you need to do is compare the wavelength you calculate to the commonly accepted range of visible wavelengths, which is 400 nm to 700 nm. The wavelength you calculate will probably be in meters, so you will need to convert it to nm, then compare.

Problem 11

Calculate the wavelength and frequency of a photon having the energy of 8.93 x 10^{10} J/mol.

Solution

1) Determine the energy of a single photon:

8.93 x 10^{10} J/mol / 6.022 x 10^{23} photon/mol = 1.4829 x 10^{-23} J/photon

2) Determine the frequency of the photon:

E = hν 1.4829 x 10^{-13} J = (6.626 x 10^{-34} J s) (ν)

ν = 1.4829 x 10^{-13} J / 6.626 x 10^{-34} J s

ν= 2.238 x 10^{20} s^{-1}

I'll leave it unrounded. If you were reporting this value to a teacher, you would report 2.24 x 10^{20} s^{-1}

3) Determine the wavelength of the photon:

$\lambda\nu$ = c

(λ) (2.238 x 10^{20} s^{-1}) = 3.00 x 10^8 m/s

λ= 3.00 x 10^8 m/s / 2.238 x 10^{20} s^{-1}

λ= 1.34 x 10^{-12} m

By the way, this is a very short wavelength. Visible light wavelengths are mostly in the 10^{-7} m region.

4) Often, the wave length is asked for in nanometers:

(1.34 x 10^{-12} m) (10^9 nm / 1 m) = 1.34 x 10^{-3} nm

Or, λ = 0.00134 nm

5) Often, the region of the electromagnetic spectrum is asked for.

Problem 12

The radioactive isotope Thallium-201 is used in medical diagnosis and treatment. A gamma ray emitted by an atom of Thallium-201 has an energy of 0.1670 million electron-volts. (1 MeV is 1 x 10^6 eV and 1 eV = 1.6022 x 10^{-19} J). What is the frequency in Hz of this gamma ray?

Solution

The first part converts the MeV value into Joules:

0.1670 MeV = 0.1670 x 10^6 eV = 1.670 x 10^5 eV

1.670 x 10^5 eV times 1.6022 x 10^{-19} J/eV = 2.675674 x 10^{-14} J

use E = hν:

2.675674 x 10^{-14} J = (6.6260755 x 10^{-34} J s) (x)

x = 4.038 x 10^{19} s^{-1}

Problem 13

An argon ion laser puts out 4.0 W of continuous power at a wavelength of 532 nm. The diameter of the laser beam is 6.2 mm. If the laser is pointed toward a pinhole with a diameter of 1.2 mm, how many photons will travel through the pinhole per second? Assume that the light intensity is equally distributed throughout the entire cross-sectional area of the beam. (1 W = 1 J/s)

Solution

1) Convert nm to m:

532 nm = 532 x 10^{-9} m = 5.32 x 10^{-7} m

2) Determine energy of one photon at this wavelength:

$E\lambda = hc$

E = [(6.626 x 10^{-34} J s) (3.00 x 10^8 m s^{-1})] / 5.32 x 10^{-7} m

E = 3.736466 x 10^{-19} J

3) Determine power output in terms of photons:

4 J s^{-1} / 3.736466 x 10^{-19} J per photon

1.07 x 10^{19} photons per second.

4) Determine decimal percent pinhole is of total area of beam:

Area = πr^2

$\pi(0.6)^2 / \pi(3.1)^2$

0.03746

5) Determine photons through pinhole in one second:

(0.03746) (1.07 x 10^{19}) = 4.01 x 10^{17}

Problem 14

Light of wavelengths shorter than 275 nm can be used to photodissociate the hydrogen molecule into hydrogen atoms in the gas phase. A 60.0 mL glass cylinder contains H_2(g) at 45.0 mtorr and 25.0° . What minimum amount of light energy must be absorbed by the hydrogen in the tube to dissociate 38.0% of the molecules?

Solution

1) Determine how many hydrogen molecules are present:

PV = nRT

45.0 mtorr = 0.0450 torr

(0.0450 torr / 760.0 torr/atm) (0.0600 L) = (n) (0.08206 L atm / mol K) (298 K)

n = 1.452788 x 10^{-7} mol

(6.022 x 10^{23} molecules/mol) (1.452788 x 10^{-7} mol) = 8.74869 x 10^{16} molecules

2) Determine 38.0%:

(0.380) (8.74869 x 10^{16} molecules) = 3.3245 x 10^{16} molecules

3) Determine energy of one photon with a wavelength of 275 nm:

$E\lambda = hc$

(E) (2.75 x 10^{-7} m) = (6.626 x 10^{-34} J s) (3.00 x 10^8 m/s)

E = 7.22836 x 10^{-19} J (per molecule of H_2)

4) Determine minimum energy required for the 38.0%:

(7.22836 x 10^{-10} J) (3.3245 x 10^{16}) = 0.0240 J

Chapter 5

Periodic Table of Elements

5.1 Important Concepts and Course Review

♠ **Key Results Concerning the Electron**
The state of an electron is completely defined by its **four quantum numbers**:
n: **principal quantum number**, where $n \geq 1$;
l: **secondary quantum number** (or azimuthal), where $0 \leq l \leq n - 1$;
m: **magnetic quantum number**, where $-l \leq m \leq +l$;
m_s: **spin quantum number**, where $m_s = \pm 1/2$.
♣ **Electron Configuration and Quantum Boxes**
Giving the **electron configuration** (or **electron structure**) of an atom means specifying the distribution of electrons in the various energy levels and sublevels of that atom in the ground state, listed in order of increasing energy. The electron configuration is advantageously completed by the representation of quantum boxes depicting the orbitals.
The rules to follow are the stability principle, Klechkowski's rule, Pauli's exclusion principle, and Hund's rule.
Stability Principle
When the atom is in its ground state, electrons occupy the lowest energy levels.

Klechkowski's Rule

The order of increasing energies of orbitals is the order of increasing values of the sum $(n + l)$. If two sublevels correspond to the same sum value $(n + l)$, the sublevel with the smaller value of n has the lower energy. This order corresponds to the order of assignment of sublevels to electrons. Experience has shown that this rule has some exceptions. The mathematical formula for Klechkowski's rule is:
ns, (n-2)f, (n-1)d, np
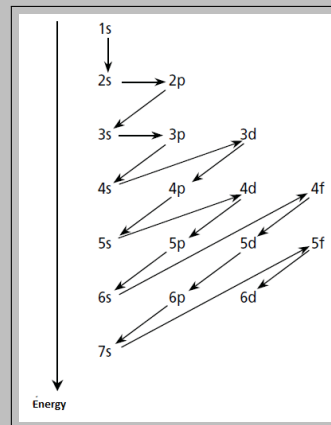
Pauli's Exclusion Principle. Quantum Boxes

Two electrons of the same atom cannot have the same four quantum numbers. This governs the representation of electrons in quantum boxes, a representation that allows the distribution of electrons based on the values of m in a given sublevel. There are as many quantum boxes as there are possible values of m; each can hold a maximum of two electrons with the same values of n, l, and m, but with opposite spins. By convention, we write $\uparrow$ for an electron with $m_s = + 1/2$ and $\downarrow$ for an electron with $m_s = - 1/2$.

Hund's Rule

In the same sublevel, the most stable configuration (i.e., the ground state) is obtained when the number of electrons with the same spin is maximal.

♣ **Periods, Groups** The periodic classification arranges elements in increasing atomic number Z, in rows called **periods**, and columns called **groups**.

A period includes all elements whose outermost sublevel s has the same energy level (the same value of n). The period is numbered with the value of n for that level. Within the period, elements are arranged iteratively based on the successive filling of ns sublevels and, depending on the atoms, $(n − 2)$f, and/or $(n − 1)$d, and/or np sublevels.

A group contains elements with the same external electron configuration. To reduce congestion, there are 18 groups rather than 32; the elements from levels $n = 6$ and $n = 7$, with incomplete f sublevels, are placed in two additional rows (lanthanides and actinides).

♣ **Evolution of Properties Within the Periodic Classification**

• Atomic radii increase when moving down the classification and from right to left. First ionization energies I_1 vary inversely with the radii.

• Element electronegativity increases when moving from bottom to top and from left to right in the classification.

• Elements on the right side of the classification tend to form anions. They are oxidizers. This property is pronounced for halogens and oxygen.

• Almost all metals tend to form cations. They are reducers. This property is pronounced for alkali metals (group 1) and alkaline earth metals (group 2).

5.2 Exercise Statements

Exercise 01

Can the quantum numbers n, l, and m_l have the following values together?
If yes, which subshells do they characterize?

	n	l	m_l			n	l	m_l
a)	2	0	0		f)	5	3	-3
b)	4	1	-2		g)	4	2	2
c)	3	1	-1		h)	2	3	3
d)	4	-1	0		i)	3	0	0
e)	2	0	-1		j)	5	2	-2

Exercise 02

Consider three elements from the 4th period, each having an outer electron configuration with 3 unpaired electrons.

1. Write the complete electron configurations of each of these elements and determine their atomic numbers.

2. Determine the atomic number and give the electron structure of the element located in the same period as iron (Z=26) and belonging to the same family as carbon (Z=6).

Exercise 03

Consider the elements: $_{29}$Cu; $_{35}$Br; $_{42}$Mo; and $_{54}$Xe.

1. Provide the electron configurations of these elements.

2. Place these elements in the periodic table.

3. Which of these elements are transition metals?

4. Which element is chemically inert, and indicate its outer structure.

5. Assign, explaining the values of first ionization energies (PI) and electronegativities of the following elements: Cu, Br, Mo.

$PI(eV)$	7.7	11.8	7.2
Electronegativity	1.9	2.8	1.8

6. An element belongs to the sixth period and group IV$_B$. What is its structure? Provide its atomic number.

Exercise 04

Consider the following elements: $_{12}$Mg; $_{27}$Co; $_{14}$Si; $_{38}$Sr

1. To which row and group do these elements belong?

2. Find the variation in radius, ionization energy, and electronegativity of these elements and classify them in ascending order.

3. What is the atomic number of the 4th transition metal of the 1st and 2nd series?

Exercise 05

1. What is the electron configuration of magnesium Mg (Z=12) in the ground state?

1.1. Is it an alkali metal? Justify.

2. Provide the 4 quantum numbers of valence electrons.

2.1. Calculate the first ionization energy.

Exercise 06

The electron configuration of the ion X^{3+} is: [Kr] $4d^{10}5s^25p^1$. Krypton is the fourth noble gas.
1. What is the atomic number of X? 2. Provide the electron configuration of the element belonging to the third period and group VI_A.

Exercise 07

1.) Provide the electron configurations of K(Z=19), F(Z=9), P(Z=15), and Cl(Z=17).

2.) The ionic compound K^+F^- has K^+ and F^- ions with practically identical radii, about 0.134 nm. What can be qualitatively inferred about the covalent radii of K and F?

3.) The covalent radius of P is 0.11 nm. What can be concluded about that of Cl?

Exercise 08

Consider the elements A, B, C, D, and E with respective atomic numbers: Z-1, Z, Z+1, 4Z/3, and 2Z-1.
Given that element D belongs to the 4th period and group VI_B:

1. Provide the electron configuration, atomic number Z, group, and period for each element.

2. Assign, for each element, the corresponding first ionization energy from the following values: 363, 100, 273, 300, 156 (Kcal/mol).

3. Rank these elements in ascending order of atomic radius.

4. Among these elements, which are transition metals? Justify.

5. What is the most electropositive element and the most electronegative element?

Exercise 09

A- Provide the configurations of the following elements and ions (corresponding Z values are indicated in parentheses): Mo(Z=42); Mg(Z=12); Zn(Z=30); In^{+++}(Z=49), Sr^{++}(Z=38).

B- Provide the first ionization energies E_{i1} in Kcal/mole for elements in the 2nd period (Z values in parentheses):

$Li(3)$	$Be(4)$	$B(5)$	$C(6)$	$N(7)$	$O(8)$	$F(9)$	$Ne(10)$
124	215	191	260	333	315	402	497

and for Group V_A

$N(7)$	$P(15)$	$As(33)$	$Sb(51)$	$Bi(83)$
333	254	231	199	185

a- Explain the variations of this quantity in this period and group. Do you observe any anomalies? Explain.

b- How can you explain that in Group V_A, the first ionization energy E_{i1} decreases less rapidly from P and even less rapidly from Sb.

c- How does atomic radius vary in this period and group?

5.3 Exercise Solutions

Exercise 01

The impossibilities are as follows:

b) m_l cannot be less than -1 since $l = 1$.

d) l can never have the value -1 (minimum: 0).

e) m_l can only be zero since $l = 0$.

h) l cannot be greater than l (maximum: n-1), and consequently, m_l cannot be equal to 3.

$\Rightarrow$ **a)** 2s - **b)** impossible - **c)** 3p - **d)** impossible - **e)** impossible - **f)** 5f - **g)** 4d - **h)** impossible - **i)** 3s - **j)** 5d.

Exercise 02

1.) An element of the 4th period $\Rightarrow$ n=4; the outermost shell is: $4s^2 3d^x 4p^y$ with 3 alone electrons $\Rightarrow 3d^3, 3d^7, \text{or } 4p^3$

♦ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3 \Rightarrow$ Z=23

↑	↑	↑		
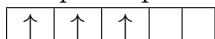
♦ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7 \Rightarrow$ Z=27

↑↓	↑↓	↑	↑	↑
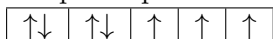
♦ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3 \Rightarrow$ Z=33

↑	↑	↑
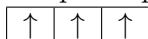
2.) $_{26}$Fe (Z=26): $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^6} \Rightarrow$ n=4 $\Rightarrow$ the element belongs to the 4th period.

The carbon family: $_6$C: $1s^2 2s^2 p^2 \Rightarrow$ Group IV$_A \Rightarrow ...4s^2 3d^{1}04p^2$

The configuration is: $1s^2 2s^2 \underline{2p^6} 3s^2 3p^6 4s^2 3d^{10} 4p^2 \Rightarrow$ Z=32

Exercise 03

Table related to questions 1 and 2

Element	Electron Configurations	Periods	Groups
Cu	$[Ar]4s^1 3d^{10}$	4	I$_B$
Br	$[Ar]\ 4s^2 3d^1 05p^5$	4	VII$_A$
Mo	$[Kr]4s^1 4d^5$	5	VI$_B$
Xe	$[Kr]5s^2 4d^{10} 5p^6$	5	VIII$_A$

3. Transition elements: Cu, Mo.

4. The most chemically inert element is: $_{54}$Xe, hence its external electron structure: $5s^2 4d^{10} 5p^6$

5. Ionization energy decreases down the column; $E_{i(Cu,Br)} > E_{i(Mo)}$

It increases across a period, so $E_{iBr} > E_{iCu}$

hence

$$
\begin{array}{ccccc}
E_{iBr} & > & E_{iCu} & > & E_{iMo} \\
11.8 & & 7.7 & & 7.2
\end{array}
$$

Electronegativity follows practically the same variation as ionization energy.

$$
\begin{array}{ccccc}
X_{Br} & > & X_{Cu} & > & X_{Mo} \\
2.8 & & 1.9 & & 1.8
\end{array}
$$

6. An element belonging to the sixth period and Group IV_B has an external electron structure: $6s^2 5d^2$.

Hence the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^2$

$$\boxed{Z=72 \;;\; {}_{72}HF}$$

Exercise 04

1.) Determination of the period and group:

Element	Electron Configuration	Period	Group
Mg	[Ne] $3s^2$	3	II_A
Co	[Ar] $4s^2 3d^7$	4	$VIII_B$
Si	[Ne] $3s^2 3p^2$	3	IV_A
Sr	[Kr] $5s^2$	5	II_A

2.)

$$
\begin{array}{cccc}
 & II_A & VIII_B & IV_A \\
3 & Mg & X & Si \\
4 & & Co & \\
5 & Sr & &
\end{array}
$$

$r_{Sr} > r_{Mg} > r_{Si}$,

$r_{Sr} > r_{Co} > r_{Si}$,

$r_{Mg} \gg r_X$,

$r_{Co} > r_X \Rightarrow r_{Mg} > r_{Co}$
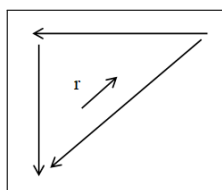
$r_{Sr} > r_{Mg} > r_{Co} > r_{Si}$

Figure 5.1: Variation of atomic radius in the periodic table

Variation in ionization energy: $IE_{Si} > IE_{Co} > IE_{Mg} > IE_{Sr}$

Electronegativity variation: $\chi_{Si} > \chi_{Co} > \chi_{Mg} > \chi_{Sr}$

3.) Transition elements:

Row 1 $ns^2(n-1)d^1$

Row 2 $ns^2(n-1)d^2$

Row 3 $ns^2(n-1)d^3$

Row 4 $\boxed{ns^2(n-1)d^4 \rightarrow ns^1(n-1)d^5}$

1st series; n=4 $\rightarrow$ $4s^1 3d^5$ (X)

2nd series; n=5 $\rightarrow$ $5s^1 4d^5$ (Y)

X: [Ar] $4s^1 3d^5 \Rightarrow Z(X) = 24$

Y: [Kr] $5s^1 4d^5 \Rightarrow Z(Y) = 42$

Exercise 05

1.) Electronic configuration of Magnesium $_{12}$Mg: $1s^2 2s^2 2p^6 3s^2$

2.) Mg is not an alkali metal because alkalis have a structure: ns^1; Mg is an _Alkaline Earth Metal_ (ns^2)

3.) The valence shell is: $3s^2$

$$
\begin{array}{ccccccc}
 & & & n & \ell & m & s \\
3s^2 & \boxed{\uparrow\downarrow} & \Rightarrow & 3 & 0 & 0 & +(1/2) \\
 & & & 3 & 0 & 0 & -(1/2)
\end{array}
$$

3.1.) First ionization energy:

Mg $\longrightarrow$ Mg$^+$ + 1e$^-$

$$IE_1 = E_f - E_i = E_{(Mg^+)} - E_{Mg}$$

Mg: $\underbrace{1s^2}_{E_1}|\underbrace{2s^2 2p^6}_{E_2}|\underbrace{3s^2}_{E_3}$ $\qquad$ Mg^+: $\underbrace{1s^2}_{E_1'}|\underbrace{2s^2 2p^6}_{E_2'}|\underbrace{3s^1}_{E_3'}$

E(Mg) $= 2E_1 + 8E_2 + 2E_3$ $\quad$ E(Mg$^+$) $= 2E_1' + 8E_2' + E_3'$

$E_1 = E_1'$ and $E_2 = E_2' \Rightarrow \boxed{IE_1 = E_3' - 2E_3}$ because $IE_1 = (\cancel{2E_1'} + \cancel{8E_2'} + E_3') - (\cancel{2E_1} + \cancel{8E_2} + 2E_3)$

$IE_1 = (\dfrac{-13.6}{9}) \times (Zeff\,^2_{Mg^+} - 2 Zeff\,^2_{Mg})$

$Zeff\,(\text{Mg}) = Z - \Sigma\sigma_i$

$Zeff\,(\text{Mg}) = 12 - [(1 \times 0.35) + (8 \times 0.85) + (2 \times 1)]$

$Zeff\,(\text{Mg}) = 2.85$

$\Rightarrow E_3 = \dfrac{(2.85)^2}{(3)^2} \times (-13.6)$

$Zeff\,(\text{Mg}^+) = 12 - [+(8 \times 0.85) + (2 \times 1)]$

$Zeff\,(\text{Mg}^+) = 3.2$

$\Rightarrow E_3' = \dfrac{(3.2)^2}{(3)^2} \times (-13.6)$

$IE_1 = \left[\left(\dfrac{(3.2)^2}{(3)^2} \times (-13.6)\right) - 2 \times \left(\dfrac{(2.85)^2}{(3)^2} \times (-13.6)\right)\right] = IE_1 = 9.074\ eV$

Exercise 06

Kr: $1s^22s^22p^63d^{10}4s^24p^6 \rightarrow$ Z=36 $\Rightarrow X^{3+}: 36 + 13 = 49$

1.) $X^{3+} + 2e^- \Longrightarrow X \Rightarrow Z(X) = 49 + 3 = 52$

2.)

$$\left.\begin{array}{l} \text{4th period} \Rightarrow n = 3 \\ \text{Group } VI_A \Rightarrow ns^2np^4 \end{array}\right\} \Rightarrow 1s^22s^22p^63s^23p^4$$

Exercise 07

1.) Electronic configuration: $_{19}$K : $1s^22s^22p^63s^23p^64s^1$

$_9$F : $1s^22s^22p^5$

$_{15}$P : $1s^22s^22p^63s^23p^3$

$_{19}$Cl : $1s^22s^22p^63s^23p^5$

2.) The cation has a smaller radius than the atom (reduction in the size of the electron cloud); the anion has a larger radius than the atom:

$r_K > 0.134$ nm

$r_F > 0.134$ nm

3.) P and Cl belong to the same period. The atomic radius decreases from left to right: $r_{Cl} < 0.11$ nm

Exercise 08

1.) D: $1s^22s^22p^63s^23p^64s^13d^5 \Rightarrow$ {n=4, Group VI$_B$ }

$\Rightarrow 4 \times \dfrac{Z}{3} = 24 \Rightarrow Z = 18$

Element	Electron Configuration	Period	Group
A: Z-1 = 18-1 =17	$1s^22s^22p^63s^23p^5$	3	VII$_A$
B: Z=18	$1s^22s^22p^63s^23p^6$	3	VIII$_A$
C: Z+1 =19	$1s^22s^22p^63s^23p^64s^1$	4	I$_A$
E: 2Z-1=35	$1s^22s^22p^63s^23p^63d^{10}4s^24p^5$	4	VII$_A$

2.) Ionization energy:

$IE_B > IE_A > IE_E > IE_D > IE_C$

3.) Ranking of elements in ascending order of atomic radius

$$r_{Ne} < r_F < r_O < r_N < r_C < r_B < r_{Be} < r_{Li} < r_N < r_P <$$
$$r_{As} < r_{Sb} < r_{Bi}$$

4.) D is a _transition metal_ because the d subshell electrons behave as valence electrons.

5.) Most electropositive: C (Alkali)

Most electronegative: A (Halogens)

Exercise 09

- A) $_{42}$Mo : [Kr] $4d^5 5s^1$; $_{12}$Mg: [Ne] $3s^2$; $_{30}$Zn : [Ar] $3d^{10} 4s^2$; $_{49}$In^{3+}: [Kr] $4d^{10}$ = $_{46}$Pd; $_{38}$Sr^{2+} = $_{36}$ Kr:[Ar] $3d^{10} 4s^2 4p^6$

-B) In a quite general manner, within the same period, *Zeff* increases from left to right $\Rightarrow$ I$_1$ increases from left to right.

- Within the same group, the radius decreases from bottom to top $\Rightarrow$ I$_1$ increases from bottom to top.
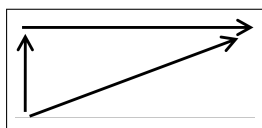
Direction of I$_1$ increase in the periodic table

Anomaly: I$_1$B < I$_1$Be, even though Z$_B$ > Z$_{Be}$ because the 2p electron in B is more easily removed than the 2s electron in Be.

Furthermore, I$_1$O < I$_1$N even though Z$_O$ > Z$_N$, because for N the half-filled p state is more stable than the p state for O containing 4 electrons (spin correlation effect).

a- I$_1$ decreases within the same group from top to bottom, but it decreases less rapidly from p onwards, and even less rapidly from Sb onwards, because for the subsequent elements after p, the d electrons and the f electrons from Sb also come into play (in the shielding effect between the nucleus and the removed electron).

d)
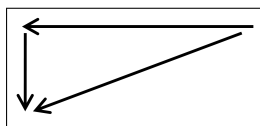
Direction of atomic radius increase in the periodic table.

$$r_{Ne} < r_F < r_O < r_N < r_C < r_B < r_{Be} < r_{Li} < r_N < r_P <$$
$$r_{As} < r_{Sb} < r_{Bi}.$$
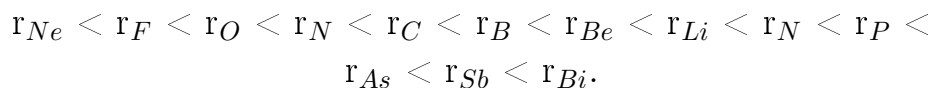
5.4   Problems

Problem 01

Give the orbital designation (1s, 2p, 3d, etc.) of electrons with the following combination of principal and azimuthal quantum numbers.

(a) n=1, ℓ=0
(b) n=2, ℓ=1
(c) n=3, ℓ=2
(d) n=5, ℓ=3
(e) n=6, ℓ=0
(f) n=4, ℓ=2

Solution

A handy guide to the ℓ values and subshell/orbital names (s, p, d, f, and so on) is this:

$$\begin{array}{c c c c c c} \ell \rightarrow & 0 & 1 & 2 & 3 & 4 \\ subshell \rightarrow & s & p & d & f & g \end{array}$$

(a) n=1, ℓ=0
n = 1 tells us that the shell number will be 1.
ℓ = 0 tells us that it will be the 's' subshell.
The orbital designation is 1s.
(b) n = 2, ℓ = 1
n = 2 tells us that the shell number will be 2.
ℓ = 1 tells us that it will be the 'p' subshell.
The orbital designation is 2p.
(c) n = 3, ℓ = 2
n = 3 tells us that the shell number will be 3.
ℓ = 2 tells us that it will be the 'd' subshell.
The orbital designation is 3d.
(d) n = 5, ℓ = 3
n = 5 tells us that the shell number will be 5.
ℓ = 3 tells us that it will be the 'f' subshell.
The orbital designation is 5f.
(e) n = 6, ℓ = 0
n = 6 tells us that the shell number will be 6.
ℓ = 0 tells us that it will be the 's' subshell.
The orbital designation is 6s.
(f) n = 4, ℓ = 2
n = 4 tells us that the shell number will be 4.
ℓ = 2 tells us that it will be the 'd' subshell.
The orbital designation is 4d.

Problem 02

For the quantum number ℓ values below, how many possible values are there for the quantum number m_ℓ?

(a) 5; (b) 3; (c) 2; (d) 1

Solution

The rule for m_ℓ is that, given the ℓ value, we start at $-\ell$ and go by integers to zero and then to $+\ell$. We can use this formula to determine how many mℓ values for a given ℓ: $2\ell + 1$.

(a) For $\ell = 5$, the m values are -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5, a total of eleven values.

(b) Seven values of mℓ resulting from $2(3) + 1 = 7$

(c) $2\ell + 1$ gives five values. The enumeration is -2, -1, 0, 1, 2.

(d) Three values (-1, 0, 1) or $2(1) + 1 = 3$

Problem 03

What does a set of four quantum numbers tell you about an electron? Compare and contrast the locations and properties of two electrons with quantum number sets (4,3,1,+1/2) and (4,3,-1,+1/2) .

Solution

The two electrons exist in the same shell (n = 4), same subshell ($\ell = 3$). The particular subshell involved is the 4f.

The two electrons are in different orbitals with the 4f subshell. We know this by the differing mℓ values.

The two electrons have the same spin (m_s=+1/2).

Problem 04

Identify the shell/subshell that each of the following sets of quantum numbers refers to.

(a) n = 2, $\ell = 1$, $m_\ell = 1$, $m_s = +1/2$
(b) n = 3, $\ell = 2$, $m_\ell = 2$, $m_s = +1/2$
(c) n = 4, $\ell = 1$, $m_\ell = -1$, $m_s = -1/2$
(d) n = 4, $\ell = 3$, $m_\ell = 3$, $m_s = -1/2$
(e) n = 5, $\ell = 0$, $m_\ell = 0$, $m_s = +1/2$

Solution

The solution procedure involves looking at the n, ℓ pairings. The m_ℓ and ms do not play a role in answering this question.

The n values tells us the first half of the answer. The ℓ values tells us the second half of the answer. Follow this guide:

$$
\begin{array}{ccccccc}
\ell \rightarrow & & 0 & 1 & 2 & 3 & 4 \\
subshell \rightarrow & & s & p & d & f & g
\end{array}
$$

(a) 2, 1 $\rightarrow$ 2p

(b) $3, 2 \rightarrow 3d$
(c) $4, 1 \rightarrow 4p$
(d) $4, 3 \rightarrow 4f$
(e) $5, 0 \rightarrow 5s$

Problem 05

Which of the following set of quantum numbers (ordered n, ℓ, m_ℓ, ms) are possible for an electron in an atom?

Select all that apply:

$$
\begin{array}{ll}
(a)3, 2, 2, -1/2 & (f)5, 3, -3, +1/2 \\
(b)2, 1, 3, +1/2 & (g)3, 1, -2, -1/2 \\
(c) -3, 2, 2, -1/2 & (h)5, 3, 0, +1/2 \\
(d)3, 3, 1, -1/2 & (i)3, 2, -1, \pm 1/2 \\
(e)3, 2, 1, -1 & (j)3, 2, -1, 0
\end{array}
$$

Solution

Let us find the correct ones by removing all the sets that are incorrect.

1) When scanning for incorrect sets, the first step is to scan the ms values. Since this value can only be +1/2 or -1/2, we can quickly remove any incorrect ones and not have to analyze their n, ℓ, and m_ℓ values.

We see that (e) with ms = -1, (i) with ms = $\pm 1/2$, and (j) with $m_s =$ violate the rule for ms. Remember, ms can ONLY be EITHER positive 1/2 or negative 1/2 in the set of four quantum numbers, not any other value. And certainly not both at the same time.

2) Next, scan for incorrect n values:
We see that (c) with n = -3 violates the rule for n.

3) Scan for problems with the relationship between n and ℓ:

In (d), there is a violation of the rule for generating permissible ℓ from the given n. When n = 3, ℓ may only take on the values of 0, 1, and 2.

4) Scan for problems with the relationship between ℓ: and m_ℓ

In (b), there is a violation of the rule for generating permissible m_ℓ from the given ℓ. When $\ell = 1$, the permitted values for m_ℓ are -1, 0, and 1. A value of 3 is not allowed. (g) shows the same mistake. When $\ell = 1$, m_ℓ cannot equal -2.

5) Examination of (a), (f), and (h) will show that these sets of quantum numbers adhere to all the rules. Verification of this is left to the student.

Problem 06

Give the maximum number of electrons in an atom that can have these quantum numbers:

(a) n = 4

(b) n = 5, m_ℓ = +1

(c) n = 5, m_s = +1/2

(d) n = 3, ℓ = 2

(e) n = 1, ℓ = 0, m_ℓ = 0

Solution

(a) n = 4

The total number of m_ℓ values (derived from all possible ℓ states for a given n value) is given by n^2. This gives us 16 m_ℓ values when n = 4. Here is a listing of the m_ℓ values when n = 4:

ℓ	m_ℓ	$Total\ m_\ell$
0	0	1
1	$-1, 0, 1$	3
2	$-2, -1, 0, 1, 2$	5
3	$-3, -2, -1, 0, 1, 2, 3$	7
4	$-4, -3, -2, -1, 0, 1, 2, 3, 4$	9

Since you also have to include ms, you multiply n^2 by 2 to get the maximum amount of electrons in the entire energy level:

$2n^2$

$2(4)^2$

32

(b) n = 5, m_ℓ = 1

The value of ℓ has not been specified; therefore, we need to take into account all the possibilities for ℓ. When n = 5, the permitted values for ℓ are 0, 1, 2, 3, 4. Let's look at each ℓ in the context of m_ℓ being equal to 1.

When ℓ = 0, m_ℓ can only equal 0. ℓ = 0 is not part of the correct answer

When ℓ = 1, m_ℓ can take on the values of -1, 0, 1. ℓ = 1 is part of the correct answer.

In like manner, ℓ = 2, 3, 4 are all part of the correct answer. Here are the m_ℓ values:

$\ell = 2$ m$_\ell$ = -2, -1, 0, 1, 2
$\ell = 3$ m$_\ell$ = -3, -2, -1, 0, 1, 2, 3
$\ell = 4$ m$_\ell$ = -4, -3, -2, -1, 0, 1, 2, 3, 4

Each ℓ value has an m$_\ell$ of 1 allowed.

Four different orbitals (n, ℓ, m$_\ell$ just below) are possible for n = 5 and m$_\ell$ = 1:

5, 1, 1   5, 2, 1   5, 3, 1   5, 4, 1

Each orbital can hold two electrons (m$_s$ = +1/2 and m$_s$ = -1/2), so the total number of electrons is 8.

(c) n = 5, m$_s$ = +1/2

The problem is very similar to (b), except that ms is given. This value corresponds to a single electron within an m$_\ell$ value. Therefore, we need to find out how many numbers of m$_\ell$ we have in order to know the number of max electrons.

Like before, ℓ = 0, 1, 2, 3, 4. Since m$_\ell$ is not specified we have to take all possible m$_\ell$ values for each ℓ value and add them together:

ℓ	$2\ell + 1$	$Total\ m_\ell$
0	$2(0) + 1$	1
1	$2(1) + 1$	3
2	$2(2) + 1$	5
3	$2(3) + 1$	7
4	$2(4) + 1$	9

Notice that the total number of m$_\ell$ states can be given by the formula $(2\ell + 1)$.

Thus, the total number of m$_\ell$ states is $(1 + 3 + 5 + 7 + 9) = 25$. This is the highest number of electrons with m$_s$ = +1/2.

You might be required to enumerate all the m$_\ell$ values as opposed to just stating how many there are using the $(2\ell + 1)$ formula. In that case:

ℓ	m_ℓ	$Total\ m_\ell$
0	0	1
1	$-1, 0, 1$	3
2	$-2, -1, 0, 1, 2$	5
3	$-3, -2, -1, 0, 1, 2, 3$	7
4	$-4, -3, -2, -1, 0, 1, 2, 3, 4$	9

(d) n $=\ell$ 3, $\ell = 2$

The only numbers not specified are m_ℓ and ms. You have to determine all the possibilities for them:
♯of $m_\ell = 2\ell + 1 = 2(2) + 1 = 5$

There will be two electrons per m_ℓ state ($m_s = +1/2$ and -1/2) therefore, maximum number of electrons is 5 x 2 = 10.

(e) n $= 1$, $\ell = 0$, $m_\ell = 0$

The only number not specified is ms. Consequently, there are only two electrons that can have the 3 values given. The quantum numbers for those two electrons are:

$$1, 0, 0, +1/2$$
$$1, 0, 0, -1/2$$

Chapter 6

Chemical Bonds

6.1   Important Concepts and Course Review

A **covalent bond** between two atoms, A and B, forms when the mutual approach of the two atoms allows for the overlap of their respective electron clouds of valence electrons and spin pairing.

♠ Lewis Model

In 1916, Lewis was the first to propose that a covalent bond results from electron sharing: two electrons for a single bond, four or six electrons for double or triple bonds, respectively.

A single covalent bond can also result from the donation of a full electron pair by a donor (having at least one lone pair) to an acceptor with an electron deficiency. This is called a **dative covalent bond** or **coordination bond**. Lewis structures are used to represent bond formation or visualize the distribution of valence electrons within neutral molecules or ions. Typically, electron pairs are represented by dashes, and lone electrons are represented by dots. We distinguish between "bonding pairs (or lone pairs)" and "non-bonding pairs (or lone pairs)."

In many cases, except for hydrogen, atoms tend to surround themselves with four electron pairs, totaling eight electrons. This gives them the electron configuration $ns^2 np^6$ of a noble gas and results in stability (**octet rule**).

♠ Stability Concept and Octet Rule

The only elements that exist in nature as isolated, free atoms are the noble gases or rare gases (Group VIII$_A$). The fact that they can remain in this form demonstrates that they are **stable**.

This stability is due to their completely filled outer shell, which contains **8 electrons** (4 pairs). The only exception is helium, which has a single filled shell with **2 electrons** (1 pair). All other elements in the periodic table have an incomplete outer shell (less than 8 electrons in the outer shell). These elements are not stable.

- **Octet Rule (Octet = Eight)** The goal of any atom with an incomplete outer shell is to acquire the **electron structure of the nearest noble gas**. To achieve this goal, it will bond with other atoms,

  - either by giving away its outer electrons to other atoms,

  - or by taking electrons from other atoms,

  - or by sharing electrons with other atoms.

♠ **Molecular Orbitals**

The concept of "overlap of electron clouds" in bond formation is replaced by the more precise concept of "combination of atomic orbitals (AOs)" (describing bonding electrons) into molecular orbitals (MOs). Each MO corresponds to two electrons with opposite spins.

The Linear Combination of Atomic Orbitals (LCAO) method is a model that calculates the molecular orbitals Ψ. According to this method, MOs have the form of a linear combination of atomic orbitals Ψ_i, which means they are a sum of first-degree terms, weighted by algebraic coefficients c_i.

$$\Psi = \sum_i c_i \Psi_i$$

The combination of N atomic orbitals results in N molecular orbitals: N/2 are bonding MOs, meaning they have lower energy than the AOs of isolated atoms, while N/2 are antibonding MOs, meaning they have higher energy than the AOs of isolated atoms. Antibonding MOs are denoted by an asterisk $*$.

The AOs Ψ_i that combine must have appropriate symmetry. We distinguish:
- overlap (or fusion) of two AOs with the same axis of symmetry, such as s orbitals or $2p_y$ orbitals, called "axial overlap." This results in two sigma (σ and σ^*) MOs.
- overlap (or fusion) of two AOs with parallel axes of symmetry, such as $2p_x$ or $2p_z$ orbitals, called "lateral overlap." This results in two pi (π and π^*) MOs. This type of overlap can only occur simultaneously with the axial overlap of $2p_y$ AOs.

♠ **Sigma (σ) and Pi (π) Bonds. Bond Order**

A single bond is necessarily a sigma (σ) bond; a double bond consists of one sigma (σ) bond and one pi (π) bond; a triple bond consists of one sigma (σ) bond and two pi (π) bonds.

Pi (π) bonds are weaker than sigma (σ) bonds. They can open up to form addition compounds, particularly observed with double or triple bonds between two carbon atoms.

♣ The geometric shape of molecules can be: (1) explained by valence bond theory (VBT) supplemented by the theory of hybridization of atomic orbitals, or (2) predicted by the VSEPR (Valence-Shell Electron-Pair Repulsion) model.

♠ Valence Bond Theory and Hybridization of Atomic Orbitals

The valence bond theory considers that a molecule is made up of a combination of bonds between atoms taken two by two. Each bond results from the overlap of AOs of bonded atoms.

♠ VSEPR Method

This predictive method is based on the postulate that areas of high electron density (bonding pairs and lone pairs) arrange themselves around an atom to minimize their mutual repulsions. A multiple bond is treated as an area of high electron density, just like a single sigma (σ) bond.

After establishing the Lewis representation of the molecule, or the part of the molecule under consideration, it is symbolized as follows: AX_mE_n; A is the central atom, X is any atom bonded to A, and E represents any non-bonding pair from A.

▲ In the VSEPR method, the geometry is determined solely by the repulsion between the doublets of the central atom. The lone pairs of the peripheral atoms are not taken into account.

▲ Multiple bonds are not considered when determining molecular geometry. They are treated as single bonds. Thus, it is not the total number of bond pairs but the number of atoms bonded to the central atom that matters. This is because we are concerned with the directions of the bonds and not their number. Whether a bond is single, double, or triple, it occupies only one direction. Therefore, the nature of the bond does not affect the determination of molecular geometry.

6.2 Exercise Statements

Exercise 01

1. Represent all the covalent bonds in the following molecules: C_2H_6, H_2CO_3, NH_3, SiH_4, NBr_3, CO_2.

2. Represent all possible covalent bond structures of the molecule C_4H_{10}.

3. Establish the corresponding molecular Lewis structures for the following formulas: ClO^-, ClO_2^-, ClO_3^-, ClO_4^-.

Exercise 02

1. Provide the Lewis representation for the molecule of phosphorus trichloride PCl_3.

2. Given that the molecule of phosphorus oxychloride ($POCl_3$) is stable, explain how the new bond between P and O is formed. Specify its nature.

3. Is the octet rule respected in cases (1 and 2)?

4. How can you explain the existence of the molecule PCl_5 but not the molecule NCl_5?

Exercise 03

The dipole moment of H_2S, hydrogen sulfide, is 0.96 D. The angle between the S-H bonds is 93° (H-S-H), and the bond length is r=1.33 Angstöm.

1. Calculate the dipole moment of the S-H bond in this molecule.

2. Calculate the partial charge on each atom in this molecule in terms of the electron charge.

3. Since the dipole moment of the CO_2 molecule is equal to 0 D, what can you deduce about the arrangement of carbon and oxygen atoms?

Exercise 04

The KCl molecule in the gaseous state has a dipole moment of 10 Debye, and the distance between the nuclei is 2.57×10^{-8} cm.

1. Is the KCl bond purely ionic?

2. If not, calculate its percentage of ionic character.

3. Determine the polarity of the bonds in H_2O, PCl_3, and Br_2.

Exercise 05

Starting from the electronic structure of each element:

1. Write the Lewis electronic structures of silicon hydride (SiH_4) and phosphine (PH_3).

2. Why doesn't aluminum hydride with the formula AlH_5 exist?

3. Propose an electronic structure for sodium borohydride $NaBH_4$ and sodium aluminohydride $NaAlH_4$ (Given Z; P=15, Si=14, Al=13, B=5, Na=11).

Exercise 06

Consider the molecule Li_2.

1. Determine the number of electrons in this molecule.

2. Place these electrons in molecular orbitals. What principle is used?

3. How does the Li-Li bond length change if the molecule is excited? Same question if the molecule is ionized?

Exercise 07

Using the energy diagram for N_2, determine for the molecules CO and NO:

1. The electron structures.

2. The number and nature of the bonds.

3. The magnetic character.

4. Arrange the following molecules in increasing order of stability: NO, NO^-, NO^+.

Given atomic numbers: $_6C$, $_7N$, $_8O$.

Exercise 08

a. Predict the type of hybridization of the central atom in the following molecules:

1. CaI_2, $GaCl_3$, H_2S, $HgCl_2$, GeH_4, NF_3.

Deduce the geometry of each molecule. **b.** Among these molecules, which ones are polar? Given atomic numbers: $_1H$, $_9F$, $_{16}S$, $_{17}Cl$, $_{20}Ca$, $_{31}Ga$, $_{32}Ge$, $_{80}Hg$.

Exercise 09

Indicate the hybridization of the carbons and heteroatoms in the following compounds:

1. H_3C——OH

2.
   H_3C with H and =O

3. CH_2==C==CH_2

4. CH_3——O——CH_3

5. CH_3——NH_2

6.
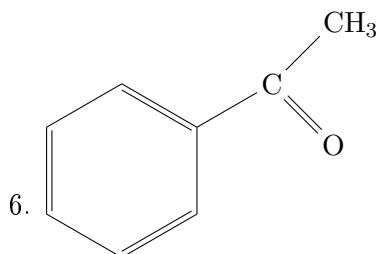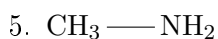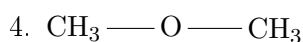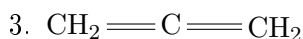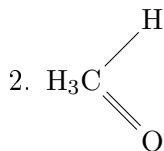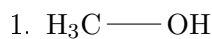
Exercise 10

Hydrazine has the following structural formula:
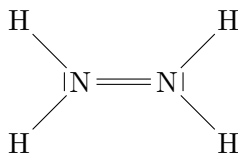
1. What is the hybridization of the nitrogen atoms? Is it the same as that of the nitrogen atom:

   (a) in ammonia;

   (b) in the ammonium ion;

   (c) in an imine with the formula RCH=N-R$'$?

   Indicate the order of magnitude of the angle H$\hat{N}$H in hydrazine.

2. Is hydrazine acidic or basic? Justify.

Exercise 11

a. Provide the electron structure of aluminum in its ground state and excited state using quantum boxes. **b.** Geometrically represent (with an explanation using the theory of hybridization of atomic orbitals) the molecule $AlCl_3$. Given atomic numbers: $_{13}Al$, $_{17}Cl$. **c.** Can the molecules $AlCl_3$ and NH_3 form the addition compound Cl_3AlNH_3? Justify your answer.

6.3 Exercise Solutions

Exercise 01

1.) Representation of Covalent Bonds
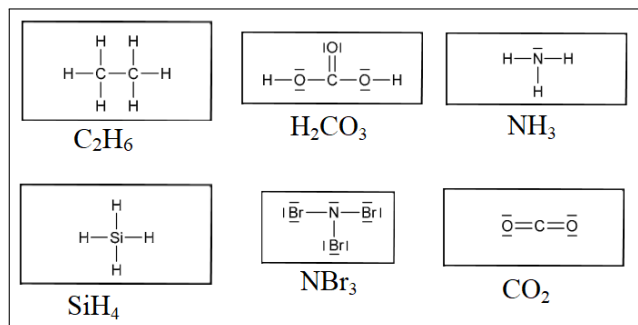
Figure 6.1: Representation of covalent bonds

2.)
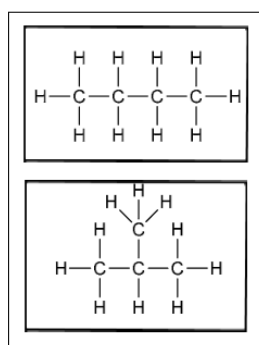
Figure 6.2: Structures and covalent bonds of C_4H_{10}

3.)
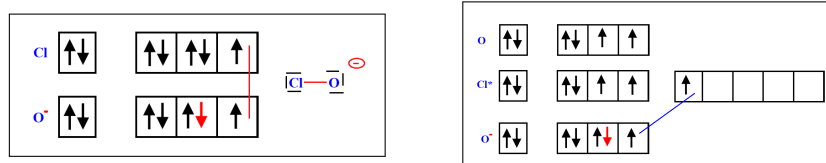
Figure 6.3: Lewis structure of ClO^- Figure 6.4: Lewis structure of ClO_2^-
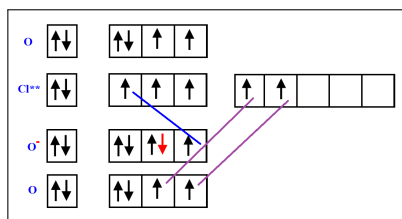
Figure 6.5: Lewis structure of ClO_3^-

Exercise 02

1.) Lewis Representation

$$\begin{array}{c} Cl \\ | \\ Cl \text{——} P \text{——} Cl \end{array}$$
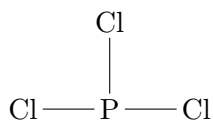
2.) Electronic structure of phosphorus $_{15}P$:

$$1s^2 2s^2 2ps63s^2 3p^3 \quad \text{(Ground state)}$$

$$1s^2 2s^2 2ps63s^1 3p^3 3d^1 \quad \text{(Excited state)}$$
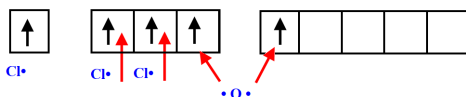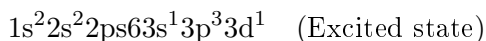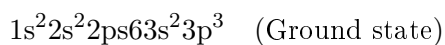
Figure 6.6: Quantum box model

Three single covalent bonds and one double bond are formed between O and P.

$$\begin{array}{c} \overset{\frown}{O} \\ \| \\ |\overline{Cl} \text{——} P \text{——} \overline{C}l| \\ \| \\ |\underline{C}l| \end{array}$$
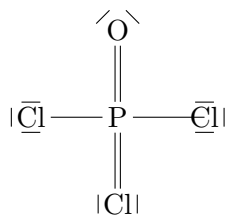
3.) The octet rule is respected in PCl_3; however, in the case of $POCl_3$, d orbitals are used, so it is not.

$$\cdot \overline{P} \cdot \xrightarrow{\text{Excitation}} \cdot \overset{\cdot\cdot}{P} \cdot$$
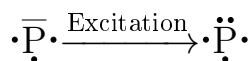
4.) Phosphorus ($_{15}P$) belongs to the third period, and d orbitals are involved (five possible bonds), which allows the existence of the PCl_3 molecule.

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In contrast, nitrogen (N) belongs to the second period (no d orbitals), and the electronic structure stops at p, allowing for three possible bonds. Therefore, NCl_5 does not exist.

Exercise 03

Since sulfur is more electronegative than hydrogen, the S-H bond is polarized. Therefore, there exists a dipole moment $\vec{\mu}_{S-H}$ directed along each S-H bond (with the convention that it goes from positive to negative charges).

1.) $|\vec{\mu}_{H_2S}| = |\vec{\mu}_{HS}| + |\vec{\mu}_{HS}|$

The dipole moment $\vec{\mu}_{H_2S}$ of the molecule is directed along the bisector of the angle $\widehat{HSH}$.

$$\cos\frac{93°}{2} = \frac{1/2|\vec{\mu}_{H_2S}|}{|\vec{\mu}_{H-S}|}$$

$$\Rightarrow |\vec{\mu}_{H-S}| = \frac{|\vec{\mu}_{H_2S}|}{2 \times \dfrac{93°}{2}} = \frac{0.96}{2 \times 0.68}$$

$$\Rightarrow \boxed{|\vec{\mu}_{H-S}| = 0.7 \text{ D}}$$

2.) The partial charge on each atom:

$$|\vec{\mu}_{H_2S}| = \delta \times \vec{l} \Rightarrow \delta = \frac{|\vec{\mu}_{H-S}|}{l} = \frac{0.7 \times 0.33 \times 10^{-29}}{1.33 \times 10^{-10}}$$

$$\delta = 0.173 \times 10^{-19} \text{ Cb}$$

So, $\delta = 0.108$ e

- The charge carried by S is equal to: 0.216 e
- The charge carried by H is equal to: 0.108 e

3.) The CO_2 molecule is linear ($\widehat{OCO} = 180°$).

$$O = C = O$$
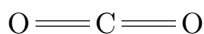
Exercise 04

1.) Let δ be the partial charge carried by each atom. The dipole moment of the bond is equal to:

$$|\vec{\mu}_{KCl}| = \delta \cdot d$$

$$\delta = \frac{|\vec{\mu}_{KCl}|}{d} = \frac{10 \times 0.33 \times 10^{-29}}{2.67 \times 10^{-10}}$$

$$\boxed{\delta = 1.236 \times 10^{19} \text{ Cb}}$$

The value of δ is different from that of e, so KCl in the gaseous state is not purely ionic.

2.) Ionic percentage of the KCl bond:

$$\% = \frac{\mu_{Exp}}{\mu_{The}} \times 100 = \frac{\delta \cdot d}{e \cdot d} \times 100$$

$$\boxed{\% = 77.25\%}$$

3.) Polarity of H_2O, PCl_3, and Br_2.

H_2O is polar because oxygen is more electronegative than hydrogen.

PCl_3 is also polar because chlorine is more electronegative than phosphorus.

Br_2 (Br-Br) is symmetrical and nonpolar.

Exercise 05

1.) The electronic structure of each element in its ground state is as follows:

$_1$H: $1s^1$

$_{14}$Si: $[Ne]3s^23p^2$

$_{15}$P: $[Ne]3s^23p^3$

Silicon (Si) is tetravalent in the compound SiH_4, and its excited state electronic structure is: $[Ne]3s^13p^3$

Representing the atoms with their valence electrons:

$$H\cdot, \qquad \cdot\overset{\displaystyle \cdot}{\underset{\displaystyle \cdot}{Si}}\cdot, \qquad \cdot\overset{\displaystyle -}{\underset{\displaystyle \cdot}{P}}\cdot$$
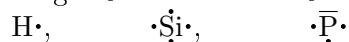
We deduce the following Lewis structures:

$$
\begin{array}{ccc}
& H & \\
& | & \\
H\!\!-\!\!Si\!\!-\!\!H & \text{and} & H\!\!-\!\!\overline{P}\!\!-\!\!H \\
& | & \\
& H & H
\end{array}
$$
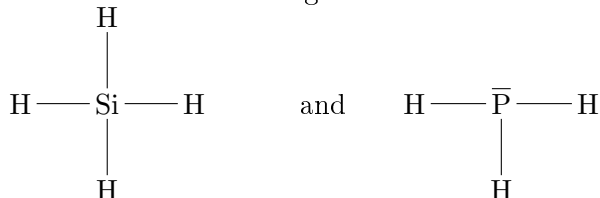
2.) $_{13}$Al: $[Ne]3s^23p^1$; the aluminum atom can have a maximum of 3 unpaired electrons in its outermost shell. Since Al cannot be pentavalent, the compound AlH_5 does not exist.

It can also be noticed that the octet rule is not satisfied for AlH_5.

3.)

$_5$B: $[He]2s^22p^1$

$_{11}$Na: $[Ne]3s^1$

Sodium (Na) belongs to the alkali metal family, and these compounds are ionic in nature. $Na^+ BH_4^-$ has the following Lewis structure:

$$
Na^+ \left[\begin{array}{c} H \\ | \\ H\!\!-\!\!B\!\!-\!\!H \\ | \\ H \end{array} \right]^-
$$
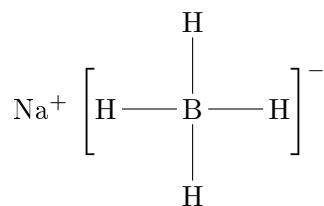
Aluminum (Al) and boron (B) are in the same group; $NaAlH_4$ can be represented as:

$$
Na^+ \left[\begin{array}{c} H \\ | \\ H\!\!-\!\!Al\!\!-\!\!H \\ | \\ H \end{array} \right]^-
$$
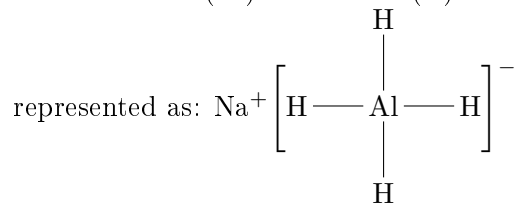
Exercise 06

1.) Number of electrons in the Li_2 molecule = 6
2.) Molecular orbital diagram of the Li_2 molecule:

Li Li_2 Li
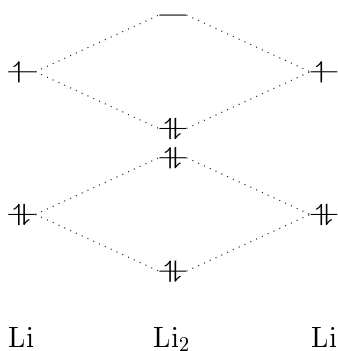
We fill the energy levels of the molecular orbitals while respecting the Pauling principle, Hund's rule, and the principle of stability.

3.) Writing the electron configuration and bond order of the Li_2 molecule in its ground state:

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \; ; \; BO(Li_2) = 1$$

Electronic configuration and bond order of Li_2 in its excited state:

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^1 \sigma_{2s}^{*1} \; ; \; BO(Li_2^*) = 0$$

Li_2^* molecule does not exist.

Electronic configuration of Li_2^+ and bond order in the ionization state:

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^1 ; BO(Li_2^+) = 0.5$$
$$BO(Li_2^+) < BO(Li_2)$$
$$\text{Therefore, L.L}(Li_2^+) > \text{L.L}(Li_2)$$

Note: O.L: Bond Order; L.L: Bond Length.

Exercise 07

1.) Energy diagram:

CO   NO
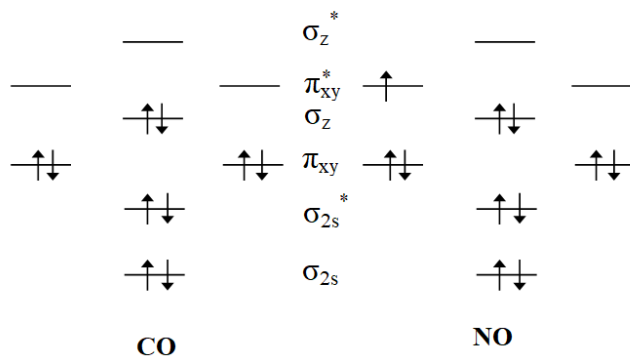
Electronic configuration: NO: $\sigma_{1s}^2\sigma_{1s}^{*2}\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{xy}^4\sigma_z^2\pi_{xy}^{*1}$ CO: $\sigma_{1s}^2\sigma_{1s}^{*2}\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{xy}^4\sigma_z^2$

2.)　　　　NO: 1 σ bond and 2 π bonds　　　CO: 1 σ bond and 1.5 π bonds

3.) Magnetic character:

The CO molecule is diamagnetic.

The NO molecule is paramagnetic.

4.) By applying the definition of bond order to NO, NO$^+$, and NO$^-$, we find the respective values: 2.5, 3, and 2.

Stability increases with bond order, so the order of increasing stability is:

$$NO^- < NO < NO^+$$

Exercise 08

a.)

Molecule	CaI_2	$GaCl_3$	H_2S	$HgCl_2$	GeH_4	NF_3
Hybridization	sp	sp^2	pseudo-sp^3	sp	sp^3	pseudo-sp^3
Geometry	Linear	Trigonal	Angular	Linear	Tetrahedral	Pyramidal

b.) A molecule is polar when its geometry and the nature of its atoms result in a non-zero vector sum of bond moments. Among these molecules, the polar ones are:

$GaCl_3$, H_2S, NF_3
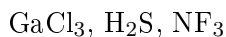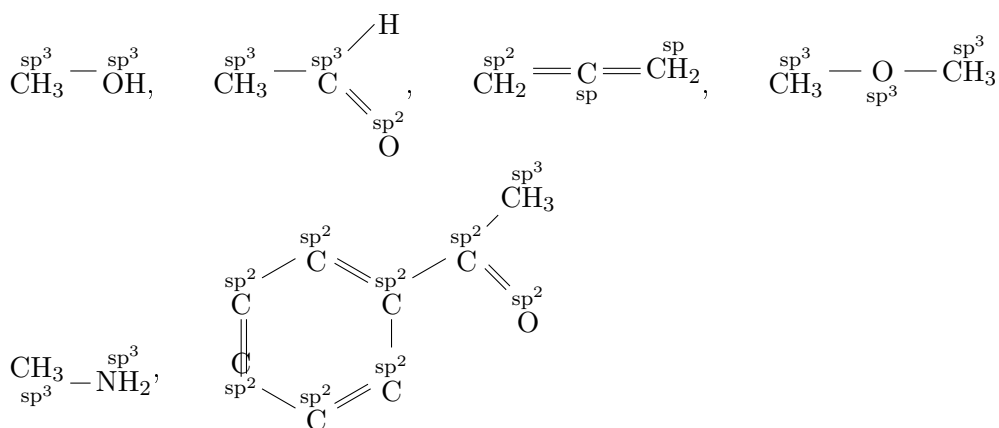
Exercise 09

Exercise 10

a.) In hydrazine, the hybridization of nitrogen atoms is sp^3.

$_7N: 1s^2\ 2s^2\ 2p^3$

sp^3
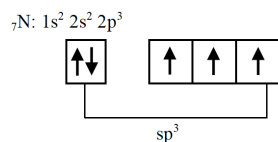
- The same type of hybridization for the nitrogen atom in NH^3 (AX_3 type) and in the NH_4^+ ion (AX_4 type). - Different hybridization in an imine: sp^2 (doublet and P_x, P_y orbitals)
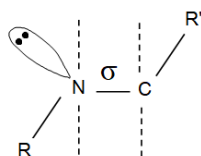
b.) Hydrazine is basic due to the presence of a lone pair on the nitrogen atom. It can capture a proton H^+.
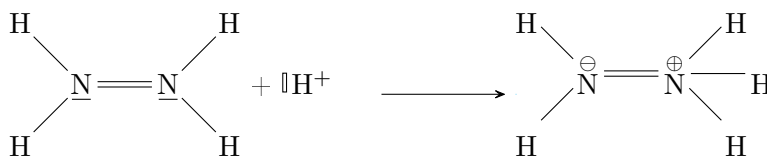
(The positive charge makes it impossible to capture a second proton).

Exercise 11

a.) Electronic structure of aluminum $_{13}Al$:

A l'état fondamental: $1s^2\ 2s^2\ 2p^63s^23p^1$

A l'état excité: $1s^2\ 2s^2\ 2p^63s^13p^2$

b.) The electronic configuration of aluminum in its ground state does not reveal the three unpaired electrons responsible for the three Al-Cl bonds. To justify the equivalence of the three Al-Cl bonds, we must consider aluminum in its excited state.

By combining the atomic orbitals (O.A.) 3s, $3p_x$, and $3p_y$ of Al, we obtain three identical sp^2 hybrid orbitals. Thus, aluminum is hybridized as sp^2. Chlorines are also hybridized as sp^2, resulting in the formation of 3 sigma (σ) bonds between the hybrid orbitals of aluminum and those of the three chlorine atoms. The remaining pure p_z orbitals are perpendicular to the plane, leading to a delocalized π system for the three doublets from the three chlorine atoms.
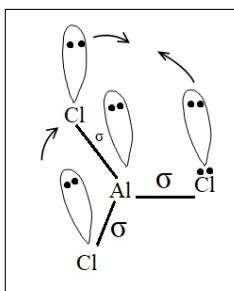
c.) The molecules $AlCl_3$ and NH_3 can combine to form the compound Cl_3AlNH_3. This is due to the vacant p_z orbital of Al and the saturated orbital of nitrogen (NH_3).
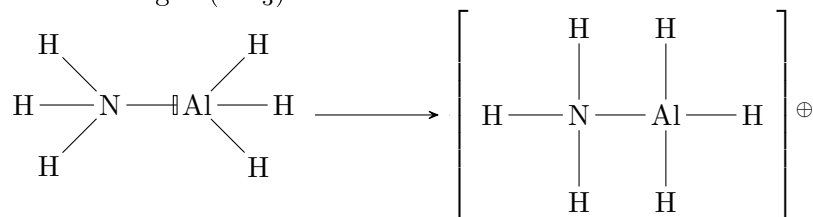
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INTERNATIONAL SYSTEM OF UNITS (SI)

SI Base Units

Base Quantity	Name	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

SI Derived Units

Derived Quantity	Name	Symbol	Equivalent SI Units
Frequency	hertz	Hz	s^{-1}
Force	newtown	N	$m \cdot kg \cdot s^{-2}$
Pressure	pascal	Pa	N/m^2
Energy	joule	J	$N \cdot m$
Power	watt	W	J/s
Electric charge	coulomb	C	$s \cdot A$
Electric potential	volt	V	W/A
Electric resistance	ohm	Ω	V/A
Celsius temperature	degree Celsius	°C	K*

*Unit degree Celsius is equal in magnitude to unit kelvin

SI Prefixes

Factor	Name	Symbol	Numerical Value
10^{12}	tera	T	1 000 000 000 000
10^{9}	giga	G	1 000 000 000
10^{6}	mega	M	1 000 000
10^{3}	kilo	k	1 000
10^{2}	hecto	h	100
10^{1}	deka	da	10
10^{-1}	deci	d	0.1
10^{-2}	centi	c	0.01
10^{-3}	milli	m	0.001
10^{-6}	micro	μ	0.000 001
10^{-9}	nano	n	0.000 000 001
10^{-12}	pico	p	0.000 000 000 001

Adapted from NIST Special Publication 811.
SI rules and style conventions recommend using spaces rather than commas to separate groups of three digits.

PERIODIC TABLE OF THE ELEMENTS