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Chapter 7

Redox Equilibria

Electron Transfers at the Heart of Life

Redox reactions are essential to bioenergetics, both for ATP production and for antioxidant defense mechanisms. These processes regulate major aspects of metabolism and have clinical implications that you will encounter regularly in your practice.
Within biological mechanisms, electron transfers play a central role in energy conversion and storage. Although not exclusive — some processes such as passive transport or osmotic equilibria operate on other principles — redox reactions support the main energy conversions that maintain cellular homeostasis.
This chapter presents the basics of this redox language, indispensable for understanding metabolism. You will learn to:

- **Track electrons** using the oxidation number
- **Understand equilibria** that regulate energy production
- **Apply these concepts** to oxidative stress, antioxidants, and specific intoxications

Whether your path leads you to medicine, pharmacy, or research, these principles will enable you to understand various physiological and pathological mechanisms, from mitochondrial respiration to contemporary therapeutic approaches.

7.1 Introduction:

Electron transfer between species

Chemical reactions are divided into two major families according to a fundamental criterion: those that involve an electron transfer between reactants, and those that do not. The former are called oxidation-reduction reactions (or redox reactions). Their technological importance is considerable, as shown by applications as diverse as metal corrosion, electroplating, battery and accumulator operation, or combustion processes.
Redox reactions are characterized by an electron transfer between chemical species, most often between a metal and a non-metal. This class of transformations usually leads to the formation of ionic compounds.
For example, the reaction between sodium and sulfur:

$$2\,\mathrm{Na(s)} + \mathrm{S(s)} \rightleftharpoons \mathrm{Na_2S(s)}$$

Similarly, the reaction between calcium and dioxygen:

$$2\,\mathrm{Ca(s)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{CaO(s)}$$

In both cases, electrons are transferred from metal atoms to non-metal atoms. Thus, the ions formed possess noble gas isoelectronic electronic structures.
The evolution of charges reflects this transfer. For example, in the reaction of sodium with sulfur:

- The sodium atom, initially neutral (charge 0), becomes a Na^+ ion (charge +1);
- The sulfur atom, initially neutral (charge 0), becomes an S^{2-} ion (charge -2).

During a classic redox reaction, such as the formation of sulfide ion from sodium and sulfur, each sodium atom will donate one electron to become a sodium ion Na^+, while the sulfur atom will capture these two electrons to form the S^{2-} ion. This electron transfer is strictly balanced: the total number of electrons lost by reducing agents must always equal the number of electrons gained by oxidizing agents, which ensures charge conservation during the reaction. This principle guides the balancing of redox equations and the determination of stoichiometric coefficients. To track these transfers, each atom is assigned an oxidation number, which corresponds to a fictitious charge evaluated according to a set of precise rules.

- In the case of simple ions, this number coincides with the charge of the ion.
- For polyatomic species, it is a convention that allows easy identification of oxidation and reduction processes, and correct balancing of reactions involving multiple types of atoms.

So what is an Oxidation Number?

7.2 Oxidation Number:

The **oxidation number** (o.n.), sometimes also referred to as the **oxidation state** (o.s.), represents the theoretical electrical charge assigned to an atom within a chemical entity, assuming that all bonds are purely ionic. This fundamental concept allows quantification of electron transfers and systematic identification of oxidizing and reducing species in a reaction.
Concretely, the oxidation number serves as our reference for tracking the path of electrons during chemical transformations. It establishes a common language for describing changes in the electronic state of atoms, from complex biological systems to the clinical applications that derive from them.

7.2.1 Rules for establishing the oxidation number

In general, it is recommended to use a method based on **Lewis** structures, where electrons are explicitly represented. It is essential to understand that the assignment of oxidation numbers is above all a system of electron accounting. These values do not represent the actual charges carried by atoms within molecules, but serve as a formal tool for analyzing electron transfers. The method based on Lewis formulas allows assigning oxidation numbers according to a structured four-step approach:
1. Representation: Write the Lewis formula of the molecule or ion under consideration.
2. Electron assignment: Assign all electrons of each bond to the most electronegative atom in that bond. Except for a bond between atoms of identical electronegativity, electrons are shared equally between the two atoms.
3. Counting: Add the total number of valence electrons assigned to each atom in the previous step.
4. Calculation: Determine the oxidation number of each element according to the following formula:

$$(\text{Oxidation Number}) = \begin{pmatrix} \text{number of valence} \\ \text{electrons of} \\ \text{the free atom} \end{pmatrix} - \begin{pmatrix} \text{number of valence} \\ \text{electrons assigned} \\ \text{to the bonded atom} \end{pmatrix}$$

Note. For **main group elements** (*s* **and** *p*), the number of valence electrons of the free atom coincides with the group number (1 to 8). This correspondence is **not valid** for transition elements, for which only the calculation of the number of valence electrons in the ground state is rigorous.

What does "Assigned valence electrons" mean? When calculating the oxidation number, a fictitious assignment of bonding electrons is made according to a simple rule: the electrons of each bond are assigned to the most electronegative atom.

The electron assignment rule:
a) For bonding electrons: the 2 electrons of a bond go entirely to the most electronegative atom. If the two atoms have the same electronegativity (bond between identical atoms), each atom receives 1 electron.
b) For non-bonding electrons (lone pairs): They remain assigned to the atom that carries them.
To better understand the concept, we will work through several examples:

1) Hydrogen

Hydrogen generally has an oxidation number of +1 in most chemical compounds, but it adopts an oxidation number of −1 in hydrides formed with alkali metals (group 1 of the periodic table, such as Li, Na, K, Rb, and Cs). This exception is explained by the ionic nature of metal hydrides, where hydrogen acts as a hydride anion (H^-), transferring its electrons to the more electropositive metals.

General case: +1 in covalent compounds Hydrogen ($\chi = 2.20$) is generally less electronegative than non-metals. It shares its electron but the bonding pair is shifted toward the partner atom, creating a partial positive charge.

Common examples:

- H_2O (water), CH_4 (methane), HCl (hydrochloric acid)
- NH_3 (ammonia), H_2SO_4 (sulfuric acid)
- CH_3OH (methanol), $C_6H_{12}O_6$ (glucose)

$$\text{o.n.(H)} = \underbrace{1}_{\text{val. e- H}} - \underbrace{0}_{\text{assigned}} = \boxed{+1}$$

Important exception: -1 in metal hydrides With very electropositive metals, hydrogen becomes the more electronegative element and captures an electron to form the hydride ion H^-.

Electronegativity comparison:

- Alkali metals: $\chi \approx 0.8 - 1.0$ (Li, Na, K ..)
- Alkaline earth metals: $\chi \approx 1.0 - 1.3$ (Mg, Ca, Ba ..)
- Hydrogen: $\chi = 2.20$

$$\text{o.n.(H)} = \underbrace{1}_{\text{val. e- H}} - \underbrace{2}_{\text{assigned}} = \boxed{-1}$$

Typical hydrides:

- NaH, LiH, KH (alkali hydrides)
- CaH_2, MgH_2, BaH_2 (alkaline earth hydrides)

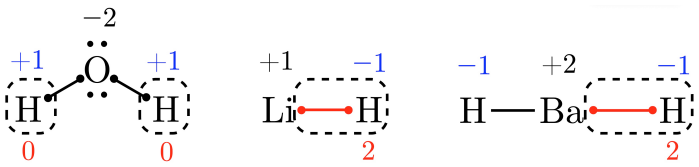


Figure 7.1 Examples of Hydrogen oxidation numbers.

How to recognize exceptions?
A compound is a metal hydride if:

- The formula begins with a metal symbol (Na, Ca, etc.)
- Followed directly by H or H_2
- Examples: NaH, CaH_2, LiH

Remember: Hydrogen: +1 except in metal hydrides: -1

2) Alkali metals

Alkali metals (Li, Na, K, Rb, Cs, Fr) always have an oxidation number of +1 in all their compounds. This is explained by their **low electronegativity**, which causes them to **easily lose** their single valence electron to form M^+ cations, thus reaching the noble gas electronic configuration.

Examples:

- NaCl: Na = +1, K_2O: K = +1, LiOH: Li = +1
- Na_2SO_4: Na = +1, $KMnO_4$: K = +1

Remember: Alkali: always one.

3) Alkaline earth metals

Alkaline earth metals (Mg, Ca, Sr, Ba, Ra), as well as zinc (Zn) and cadmium (Cd), always have an oxidation number of +2 in all their compounds. Their **low electronegativity** favors the **complete loss** of their two valence electrons, forming M^{2+} cations with a stable electronic configuration.

Alkaline earth metal examples:

MgO: Mg = +2	$SrSO_4$: Sr = +2	$ZnSO_4$: Zn = +2	CdS: Cd = +2
$CaCl_2$: Ca = +2	$Ba(OH)_2$: Ba = +2	$ZnCl_2$: Zn = +2	CdO: Cd = +2

Remember: Alkaline earth: always two.

4) Fluorine:

From electron-donating metals to fluorine, the ultimate acceptor

After studying alkali and alkaline earth metals, characterized by their **low electronegativity** that leads them to **lose** their valence electrons easily (constant positive O.N.), we now turn to the extreme opposite: **fluorine**, the most electronegative element in the periodic table. While metals tend to form cations, fluorine exhibits an **exceptional electron affinity** that systematically leads it to **capture** an electron, explaining its radically different behavior and its characteristic oxidation number of −1 in all its compounds.

Fluorine invariably has the oxidation number −1 in all its compounds. As the most electronegative element in the periodic table ($\chi \approx 4.0$), it always attracts bonding electrons toward itself, without any exception. This absolute constancy makes it a unique case among the halogens.

Examples:

- **Ionic compounds**: NaF (sodium fluoride): F = −1; CaF_2 (calcium fluoride): F = −1
- **Covalent compounds**: HF (hydrofluoric acid): F = −1; CF_4 (carbon tetrafluoride): F = −1
- **With other halogens**: ClF_3 (chlorine trifluoride): F = −1, Cl = +3; BrF_5 (bromine pentafluoride): F = −1, Br = +5

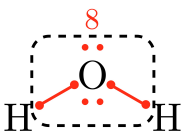
Remember: Fluorine: always -1 in its compounds

5) Oxygen: From fluorine, the most electronegative element, to oxygen, its closest rival.

After examining fluorine, which systematically imposes the oxidation number −1 thanks to its maximum electronegativity, we now turn to the element that directly follows it: oxygen. Although slightly less electronegative than fluorine ($\chi \approx 3.5$ vs. 4.0), it retains a strong tendency to attract electrons, but with more varied behaviors than fluorine. Its most characteristic oxidation number remains −2, as illustrated by the fundamental example of water.

Calculation of the oxidation number of oxygen in H_2O:
The water molecule H_2O: oxygen forms two O–H bonds (a total of 4 bonding electrons). Since oxygen is more electronegative than hydrogen, the 4 bonding electrons are assigned to it. Adding the 4 non-bonding electrons (2 lone pairs), we obtain a total of 8 electrons assigned to oxygen. Compared to its neutral state (6 valence electrons), oxygen has thus gained 2 electrons, corresponding to the oxidation number −2.

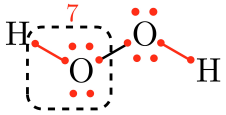
$$\text{o.n.(O)} = \underbrace{6}_{\text{val. e- O}} - \underbrace{8}_{\text{assigned}} = \boxed{-2}$$



Examples of oxides and oxygenated compounds: H_2O (water), CO_2 (carbon dioxide), Fe_2O_3 (iron(III) oxide), SiO_2 (silica), CaO (quicklime), Al_2O_3 (alumina), SO_2 (sulfur dioxide), P_4O_{10} (phosphoric anhydride)
However, some notable exceptions must be remembered:

- **Peroxides** (presence of an O–O bond): in these compounds, each oxygen carries an oxidation number −1. This particularity is explained by the sharing of two electrons between two oxygen atoms, which are therefore not fully reduced. Calculation of the oxidation number:

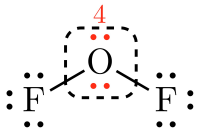
$$\text{o.n.(O)} = \underbrace{6}_{\text{val. e- O}} - \underbrace{7}_{\text{assigned}} = \boxed{-1}$$



Examples of Peroxides: They are quickly identified in the structural formula. H_2O_2 (hydrogen peroxide), Na_2O_2 (sodium peroxide), BaO_2 (barium peroxide), K_2O_2 (potassium peroxide).

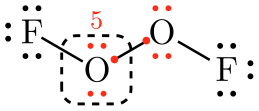
- **Fluorinated compounds**: When oxygen is bonded to fluorine (the most electronegative element), it adopts a positive oxidation number, because it is fluorine that attracts the electrons. In fluorides, oxygen is placed after fluorine in the chemical formula. in oxygen fluoride OF_2, oxygen is at +2.

$$\text{o.n.(O)} = \underbrace{6}_{\text{val. e- O}} - \underbrace{4}_{\text{assigned}} = \boxed{+2}$$



And for O_2F_2 dioxygen difluoride, the o.n. of oxygen is +1.

$$\text{o.n.(O)} = \underbrace{6}_{\text{val. e- O}} - \underbrace{5}_{\text{assigned}} = \boxed{+1}$$

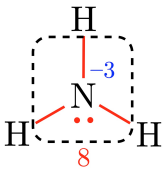


Remember: Oxygen: −2 except peroxides (−1), or dominated by F (positive)

Note: Mastering these exceptions allows avoiding classic mistakes in oxidation number determination exercises and understanding redox reaction mechanisms well. The rules presented are consistent with IUPAC convention (Nomenclature of Inorganic Chemistry, 2005/2013).

6) **Nitrogen:** For this atom, let us take the ammonia molecule as an example: it has three N-H bonds (6 bonding electrons). Since nitrogen is more electronegative than hydrogen, the 6 bonding electrons are assigned to nitrogen. Adding the 2 non-bonding electrons (1 lone pair), nitrogen therefore has 8 assigned electrons in the molecule, whereas it has 5 valence electrons in the isolated state.
Calculation of the oxidation number:

$$\text{o.n.(N)} = \underbrace{5}_{\text{val. e- N}} - \underbrace{8}_{\text{assigned}} = \boxed{-3}$$



Examples for N at -3: NH_3 (ammonia), NH_4^+ (ammonium ion), CH_3NH_2 (methylamine), NaN_3 (sodium azide - central atom), urea (urea).

Nitrogen often takes the oxidation number −3 when bonded to less electronegative elements such as hydrogen or metals, ($\chi_N = 3.04$) and captures electrons from bonds.

However, nitrogen exhibits a wide variety of oxidation numbers:

- $\boxed{-2}$: N_2H_4 (hydrazine)
- $\boxed{-1}$: NH_2OH (hydroxylamine)
- $\boxed{0}$: N_2 (dinitrogen)
- $\boxed{+1}$: N_2O (nitrous oxide)
- $\boxed{+2}$: NO (nitric oxide)
- $\boxed{+3}$: N_2O_3 (dinitrogen trioxide), NO_2^- (nitrite)

+4: NO_2 (nitrogen dioxide) +5: N_2O_5 (dinitrogen pentoxide), NO_3^- (nitrate)

Compounds with oxygen: Since oxygen is more electronegative, nitrogen's oxidation number becomes positive.

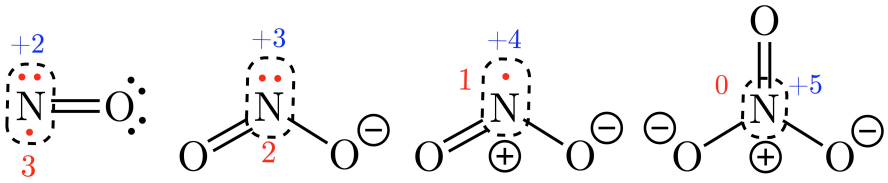


Figure 7.2 Other examples of positive oxidation numbers of nitrogen

How to determine the oxidation number?

For nitrogen, the oxidation number depends mainly on:
- Bonding partners
- Relative electronegativity
- Type of compound (organic or inorganic)

Note: The wide variety of nitrogen oxidation numbers explains its chemical richness in organic, biological, and environmental chemistry. This versatility is crucial for understanding biogeochemical cycles and natural redox processes.

7) Halogens (F, Cl, Br, I)

After studying fluorine "the chief," oxygen "the deputy chief," which mainly presents the oxidation number -2, we now turn to the rest of the halogens. These group 17 elements mainly have the oxidation number -1 in their compounds, but can also adopt positive oxidation numbers when bonded to more electronegative elements (oxygen, fluorine). Their behavior varies according to their position in the group: while fluorine systematically imposes -1 thanks to its maximum electronegativity, the other halogens (Cl, Br, I) show a diversity of oxidation numbers.
- **Fluorine**: exclusively -1 (most electronegative element)
- **Chlorine, Bromine, Iodine**: predominantly -1, but also $+1$, $+3$, $+5$, $+7$ in oxyanions and compounds with oxygen

Examples:
- **Oxidation number** -1 (the most common):
  - NaCl: Cl $= -1$, HBr: Br $= -1$, KI: I $= -1$
  - $CaCl_2$: Cl $= -1$, $AlBr_3$: Br $= -1$
- **Positive oxidation numbers** (with oxygen):
  - $+1$: $HClO$ (hypochlorous acid), $NaClO$ (sodium hypochlorite)
  - $+3$: $HClO_2$ (chlorous acid), $NaClO_2$ (sodium chlorite)
  - $+5$: $HClO_3$ (chloric acid), $KClO_3$ (potassium chlorate)
  - $+7$: $HClO_4$ (perchloric acid), $NaClO_4$ (sodium perchlorate)

Remember: Halogens: -1 (majority), but also +1, +3, +5, +7

8) Total charge rule

The sum of oxidation numbers in a species equals its total charge. This rule is essential for calculating unknown O.N. values.

Key examples:

- H_2O: $2(+1) + (-2) = 0$
- NH_4^+: $(-3) + 4(+1) = +1$
- SO_4^{2-}: $(+6) + 4(-2) = -2$

Remember: Σ o.n = total charge

9) Fundamental rules

- **Free element**: O.N. = 0 (O_2, Fe, S_8)
- **Monoatomic ion**: O.N. = charge ($Na^+ = +1$, $Cl^- = -1$)
- **Total charge**: Σ O.N. = charge of the species
- **Electronegativity**: The most electronegative element in a compound has the negative O.N.

To calculate the oxidation number of an atom:

a) Count the **bonding electrons** by assigning them to the **more electronegative** atom
b) Add the **non-bonding electrons** (lone pairs)
c) Subtract from the number of valence electrons: **o.n. =** e^- **valence -** e^- **assigned**

In essence: The oxidation number transforms electronic complexity into precise accounting in the service of chemical prediction

"True mastery does not lie in memorizing rules, but in understanding their underlying electronic logic."
– Approach inspired by Lewis-Pauling pedagogy

Caution

For transition metals, the electron assignment method (based on electronegativity) is not practical. We mainly use the **algebraic method** relying on:

a) The rules for O, H, etc. (already covered)
b) The total charge constraint
c) Knowledge of the common oxidation states of each metal

Detailed calculation of the oxidation number for a transition metal: So far, we have applied systematic rules based on electronegativity for main group elements. However, **transition metals** have a fundamental peculiarity: their electronic configuration involving *d* orbitals makes the electron assignment calculation much less straightforward.
Unlike s and p elements where the number of valence electrons corresponds to the group number, transition metals require a different approach: the **total charge rule** becomes our main tool here, combined with knowledge of the usual oxidation states of each metal.

7.2.1.1 Calculation of the oxidation number of transition metals:

This section aims to explain how to determine the oxidation number (o.n.) of transition metals, both in their simple ions and in their compounds. Two complementary approaches are presented: the **general algebraic method** (applicable to all elements) and the **electronic configuration approach** (particularly useful for interpreting the behavior of transition metals).

Fundamental principle: The **oxidation number** represents the **formal (conventional) charge** that an atom would have if all its bonds with different atoms were considered purely ionic (bonding pairs are assigned to the most electronegative atom). **Note:** the oxidation number is **not** a real measurable charge on the atom; it is an **electron accounting** tool useful for tracking electron transfers.
An atom in its elemental state (uncombined) has an oxidation number of zero (0). A monoatomic ion has an oxidation number equal to its charge: thus, Na^+ has an o.n. of $+1$, Cl^- of -1, etc.
From an electronic perspective, the loss of electrons leads to cations and corresponds to a positive oxidation number; conversely, the gain of electrons gives anions and corresponds to a negative oxidation number.

General rules in compounds: To determine an oxidation number (o.n.) in a chemical species, the following rules are used:

- An element in its elemental state (e.g., Fe(s), O_2, Cl_2) has an o.n. equal to 0.
- A monoatomic ion has an o.n. equal to its charge (e.g., Fe^{3+}: +3; S^{2-}: −2).
- In a neutral compound, the sum of the oxidation numbers of all atoms is zero.
- In a polyatomic ion, this sum is equal to the total charge of the ion.
- Some elements have almost constant values:
  - Fluorine has an o.n. of −1 in its compounds.
  - Oxygen generally has an o.n. of −2, except in peroxides (−1) and in compounds with fluorine (e.g., OF_2, where O is +2).
  - Hydrogen generally has an o.n. of +1, except in metal hydrides (e.g., NaH, where H is −1).
  - Alkali metals (group 1) are generally at +1, and alkaline earth metals (group 2) at +2, in their compounds.

These rules allow writing a balance equation (sum of o.n. weighted by indices) whose unknown is the desired oxidation number.

Algebraic calculation method: The general approach is summarized to determine the oxidation number of an atom in a polyatomic species:

a) assign the known oxidation numbers (O, H, group 1 and 2 metals, halogens, etc.) to the other atoms;
b) write an equation expressing that the **sum of oxidation numbers** equals the **total charge** of the species;
c) solve this equation to obtain the unknown oxidation number;
d) **Verify** that the final sum of oxidation numbers (taking stoichiometric indices into account) indeed equals the total charge of the species.

Example (1): Iron oxide, Fe_2O_3. In Fe_2O_3, oxygen is −2. Let x be the o.n. of iron; the species being neutral:

$$2x + 3(-2) = 0 \quad \Rightarrow \quad 2x - 6 = 0 \quad \Rightarrow \quad x = +3.$$

Thus, iron (Fe) is in the oxidation state: $+3$.

Example (2): Permanganate ion, MnO_4^-:
In MnO_4^-, oxygen is −2. Let x be the o.n. of manganese; the total charge is −1:

$$x + 4(-2) = -1 \quad \Rightarrow \quad x - 8 = -1 \quad \Rightarrow \quad x = +7.$$

Thus, manganese (Mn) is in the oxidation state: $+7$.

Example (3): Dichromate ion, $Cr_2O_7^{2-}$:
In $Cr_2O_7^{2-}$, oxygen is −2. Let x be the o.n. of chromium; the total charge is −2:

$$2x + 7(-2) = -2 \quad \Rightarrow \quad 2x - 14 = -2 \quad \Rightarrow \quad 2x = 12 \quad \Rightarrow \quad x = +6.$$

Thus, chromium (Cr) is in the oxidation state: $+6$.

Example (4): Magnetite, Fe_3O_4:
In Fe_3O_4, oxygen is −2. Let x be the *average* o.n. of iron; the species being neutral:

$$3x + 4(-2) = 0 \quad \Rightarrow \quad 3x - 8 = 0 \quad \Rightarrow \quad x = +\frac{8}{3}.$$

This fractional value indicates a mixture of oxidation states: Fe_3O_4 can be seen as a mixed oxide $FeO \cdot Fe_2O_3$, containing one iron(II) (Fe^{2+}) and two irons(III) (Fe^{3+}). (a quick check: (+2) + 2(+3) + 4(-2) = 0)

Oxidation number and electronic configuration: For transition metals, the oxidation number can take multiple values. In practice, the oxidation number of an atom in an ion or molecule is **determined by the algebraic method** (charge balance, usual rules).
The electronic configuration is not used to calculate the oxidation number; it is used to interpret it.
The electronic configuration of the metal thus constitutes an **interpretive tool**: it allows associating a given oxidation number with a d^n configuration and explaining the relative stability of certain states (e.g., d^0, d^5, d^{10} configurations are frequently favored).

Valence electrons of transition metals

Transition metals have valence electrons in the ns and $(n-1)d$ subshells. During cation formation:
- the ns electrons are lost first;
- then, if necessary, $(n-1)d$ electrons are removed.

Thus, for a given metal, each oxidation number corresponds to a d^n **configuration** of the metal ion.

Recommended approach: first determine the oxidation number by the algebraic method, then deduce the electronic configuration of the ion and its d^n state.

Example: iron(II) and iron(III)

Neutral iron has the ground state configuration: Fe : $[\mathrm{Ar}]\,4s^2\,3d^6$.
- For the Fe^{2+} ion (o.n. $= +2$): loss of the two $4s$ electrons, $Fe^{2+} : [\mathrm{Ar}]\,3d^6$ (d^6).
- For the Fe^{3+} ion (o.n. $= +3$): loss of the two $4s$ electrons and then one $3d$ electron, $Fe^{3+} : [\mathrm{Ar}]\,3d^5$ (d^5).

We observe that the $+3$ state corresponds to a **half-filled** $3d$ subshell (d^5), which contributes to its stability.

Example: copper(I) and copper(II)

Neutral copper has the configuration: Cu : $[\mathrm{Ar}]\,3d^{10}\,4s^1$.
- For the Cu^+ ion (o.n. $= +1$): loss of the $4s$ electron, $Cu^+ : [\mathrm{Ar}]\,3d^{10}$ (d^{10}).
- For the Cu^{2+} ion (o.n. $= +2$): loss of the $4s$ electron and one $3d$ electron, $Cu^{2+} : [\mathrm{Ar}]\,3d^9$ (d^9).

The $+1$ state leads to d^{10}, i.e., a **full** d subshell, which explains its relative stability (although copper(I) is often unstable in aqueous solution compared to Cu(II) under certain conditions).

4. Interpretive role of electronic configuration

Examination of the electronic configuration allows:

a) **Understanding the variability of oxidation numbers**
Transition metals can successively lose the ns electrons, then some $(n-1)d$ electrons. This explains the existence of multiple oxidation states for the same element (e.g., Fe^{2+}/Fe^{3+}, Cu^+/Cu^{2+}, $Mn^{2+}/Mn^{4+}/Mn^{7+}$, etc.).

b) **Interpreting the stability of certain oxidation states**
Some oxidation numbers lead to particularly stable d subshells:
- d^0: empty d subshell (e.g., Cr(VI), Mn(VII));
- d^5: half-filled d subshell (e.g., Fe(III), Mn(II));
- d^{10}: full d subshell (e.g., Zn(II), Cu(I)).

These considerations illuminate the chemistry of transition metals in areas such as complexation, magnetism, spectroscopy, and inorganic biochemistry. However, they **do not replace** the algebraic method for determining oxidation numbers in practical exercises.

Conclusion:

In practice, the calculation of the oxidation number in a compound relies first on the **algebraic method**, based on general rules and the equality "sum of o.n. = total charge." The study of the **electronic configuration** then verifies and interprets this result, linking the oxidation state to the distribution of valence electrons. This dual approach — algebraic and electronic — allows moving from a formal number to a structuring physical reality, particularly for transition metals.

7.2.2 The usefulness of the oxidation number:

Beyond simple calculation exercises, mastery of the oxidation number is an indispensable tool for:
- **Identifying oxidation-reduction (redox) reactions**: A reaction is redox if the oxidation numbers of at least two atoms change.
- **Determining the oxidizing and reducing agents**:
  - The **oxidizing agent** is the species that **contains the atom** whose o.n. **decreases** (it is reduced).
  - The **reducing agent** is the species that **contains the atom** whose o.n. **increases** (it is oxidized).
- **Balancing redox equations** via the oxidation number method.

- **Understanding compound stability** and predicting possible reactions in biology, geochemistry, or materials science.

Concrete example: Reaction between Zinc and hydrochloric acid

$$\mathrm{Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)}$$

- **O.N. analysis:**
  - Zn: from 0 (metal) to +2 in $\mathrm{ZnCl_2}$ → o.n. increases → **Oxidation**
  - H in HCl: from +1 to 0 in $\mathrm{H_2}$ → o.n. decreases → **Reduction**
- **Conclusion:**
  - Zn is the **reducing agent** (it is oxidized)
  - HCl is the **oxidizing agent** (it is reduced)

In summary, the oxidation number is the **common thread** that allows tracking the path of electrons, offering a unified and quantitative vision of chemical transformations at the heart of matter and life.

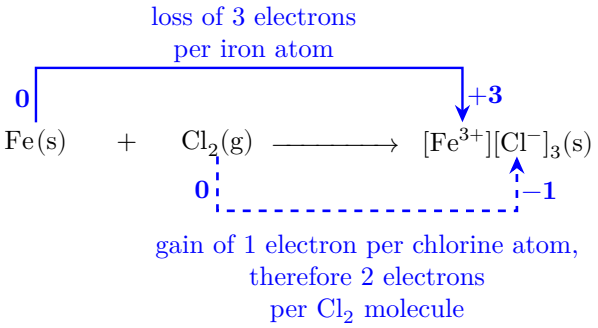
7.2.2.1 Balancing redox reaction equations:

Let us now address the balancing of redox reaction equations. To do this, we will use the **oxidation number method**. This technique is based on a fundamental principle: the total number of electrons donated by the reducing agent must be strictly equal to the total number of electrons gained by the oxidizing agent. This is the **principle of electron conservation**. By analyzing changes in oxidation numbers, we can apply this principle to balance any redox reaction. Let us illustrate this immediately with the following concrete example:

Example 1: Chlorination reaction of Iron

$$\mathrm{Fe\,(s) + Cl_2\,(g) \longrightarrow FeCl_3\,(s)} \tag{1}$$

The equation is identified as a redox reaction based on changes in oxidation numbers: iron (Fe) is oxidized (from 0 to +3) while chlorine (Cl) is reduced (from 0 to −1). These changes are schematized below, with the numbers beside the arrows representing the **oxidation states**. One iron atom (Fe) releases **3 electrons** during its oxidation, while one chlorine molecule ($\mathrm{Cl_2}$) gains **2** during its reduction (i.e., one electron per chlorine atom). To respect the principle of electron conservation, the total number of electrons donated by the **reducing agent** (Fe) must equal the total number of electrons accepted by the **oxidizing agent** ($\mathrm{Cl_2}$).



The least common multiple (**LCM**) of 3 and 2 is 6, meaning that the overall electron transfer must involve 6 electrons.

Thus, to balance this transfer:

- 2 Fe atoms (2 × 3 electrons = 6 electrons donated)
- 3 $\mathrm{Cl_2}$ molecules (3 × 2 electrons = 6 electrons gained)

These multiplications give us the **stoichiometric coefficients** of the reactants. We then obtain the following equation, which is not yet completely balanced:

$$\mathrm{2\,Fe\,(s) + 3\,Cl_2\,(g) \longrightarrow FeCl_3\,(s)} \tag{2}$$

Noting that the introduction of two Fe atoms must necessarily lead to the formation of two formula units of $\mathrm{FeCl_3}$ (principle of iron atom conservation), we place a coefficient 2 in front of $\mathrm{FeCl_3}$:

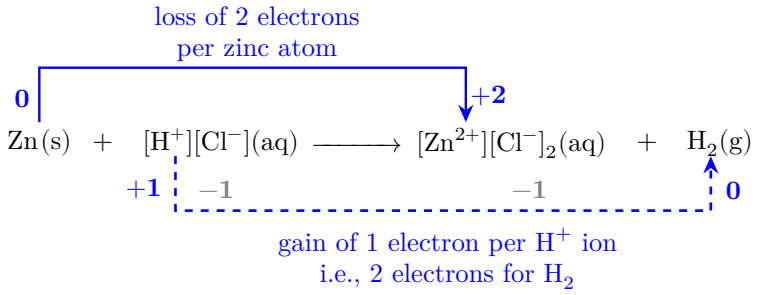
$$\mathrm{2\,Fe(s) + 3\,Cl_2(g) \longrightarrow 2\,FeCl_3(s)} \tag{3}$$

This stoichiometric coefficient also ensures chlorine atom conservation. The equation is now perfectly balanced.

Example 2: Reaction of zinc with hydrochloric acid Let us illustrate the method with a fundamental reaction:

$$\mathrm{Zn\,(s) + HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)} \tag{4}$$

The equation shows changes in oxidation numbers: zinc (Zn) is oxidized (from 0 to +2) while **hydrogen** (H) is reduced (from +1 in H^+ to 0 in H_2). **Note**: chlorine does not participate in the redox exchange; its oxidation number remains at −1 in all compounds.



One zinc atom releases **2 electrons** during its oxidation, while one hydrogen ion H^+ gains **1 electron**. The LCM of 2 and 1 is 2.
Thus:

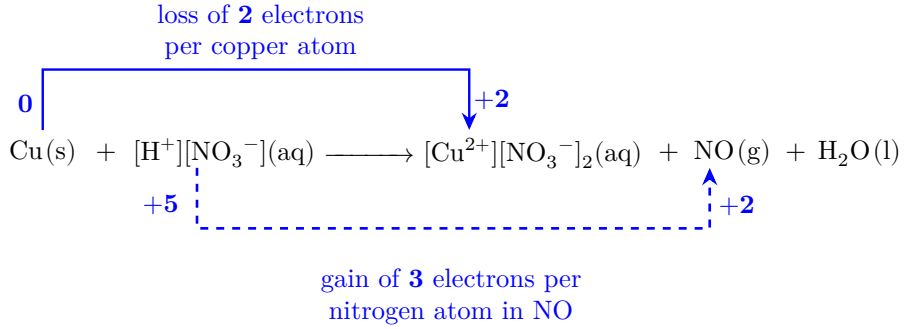
- 1 Zn atom (1×2 electrons = 2 electrons donated)
- 2 H^+ ions (2×1 electron = 2 electrons gained)

The balanced equation is:

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)} \tag{5}$$

Example 3: Reaction of copper with nitric acid Consider a more complex reaction:

$$\mathrm{Cu\,(s) + HNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + NO\,(g) + H_2O\,(l)} \tag{6}$$



Changes in oxidation numbers:

- Cu: $0 \to +2$ (oxidation) $\Leftrightarrow$ loss of **2** electrons.
- N in HNO_3: $+5 \to$ N in NO: $+2$ (reduction) $\Leftrightarrow$ gain of **3** electrons.
- N in NO_3^- (from $Cu(NO_3)_2$): +5 (no change)

Electron exchange by the oxidation number method:
The LCM of the number of electrons lost by Cu (2) and gained by N (3) is 6. Thus, we must have:

- **3 Cu atoms** (donating $3 \times 2 = 6\ e^-$)
- **2 N atoms** that are reduced (gaining $2 \times 3 = 6\ e^-$)

Half-reactions:

- Oxidation: $3 \times (\mathrm{Cu \longrightarrow Cu^{2+} + 2\,e^-})$
- Reduction: $2 \times (\mathrm{NO_3^- + 4\,H^+ + 3\,e^- \longrightarrow NO + 2\,H_2O})$

Balancing by inspection:

- The 2 reduced N atoms come from 2 HNO_3 molecules
- 6 additional NO_3^- are needed to form $3\,Cu(NO_3)_2$
- These 6 NO_3^- come from 6 additional HNO_3 molecules
- Total HNO_3: 2 (for reduction) + 6 (for counter-ions) = 8
- The H from 8 HNO_3 will form 4 H_2O

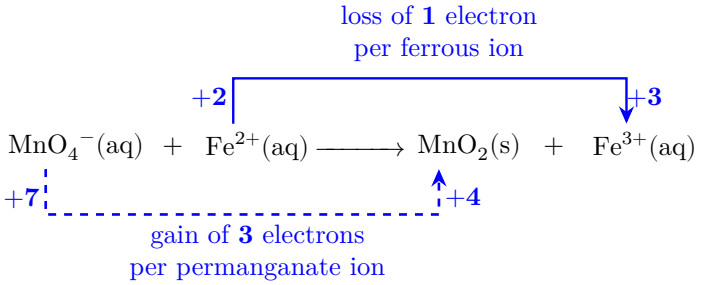
$$\boxed{3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O} \tag{7}$$

Verification:

	Left		Right
Cu	3	→	3
H	8	→	$4 \times 2 = 8$
N	8	→	$3 \times 2 + 2 = 8$
O	$8 \times 3 = 24$	→	$3 \times 6 + 2 + 4 = 24$
Charge	0	→	0

Example 4: Reaction of permanganate ions with ferrous ions in basic medium The oxidation number method also applies in basic medium. The main difference lies in balancing oxygen and hydrogen.
Consider the following reaction:

$$MnO_4^-\,(aq) + Fe^{2+}\,(aq) \longrightarrow MnO_2\,(s) + Fe^{3+}\,(aq) \tag{8}$$



Half-reaction:

- Mn in MnO_4^-: $+7 \rightarrow +4$ in MnO_2 $\Leftrightarrow$ gain of **3** electrons. Therefore we have a Reduction:

  Note:
  - On the left, one mole of MnO_4^- contains 4 oxygen atoms.
  - On the right, one mole of MnO_2 contains 2 oxygen atoms.
  - To balance oxygen in basic medium, proceed as follows:
    - Add 2 molecules of H_2O on the left to provide the 2 missing oxygen atoms on the right.
    - This introduces 4 hydrogen atoms on the left.
    - To balance these hydrogens, add 4 OH^- ions on the right.
  - The charge is balanced: left $= -1 - 3 = -4$; right $= -4$ (from the 4 OH^-).

  So this is a reduction in basic medium:

$$MnO_4^- + 2\,H_2O + \mathbf{3}\,e^- \longrightarrow MnO_2 + 4\,OH^-$$

- Fe: $+2 \rightarrow +3$ $\Leftrightarrow$ loss of **1** electron. With iron we have an oxidation:
  $Fe^{2+} \longrightarrow Fe^{3+} + \mathbf{1}\,e^-$

In basic medium, balancing requires the use of water molecules (H_2O) and hydroxide ions (OH^-) rather than hydrogen ions (H^+).

Overall reaction:

- Oxidation: $3 \times (Fe^{2+} \longrightarrow Fe^{3+} + e^-)$
- Reduction: $1 \times (MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-)$

- Balance:

$$\boxed{\mathrm{MnO_4^-\,(aq) + 3\,Fe^{2+}\,(aq) + 2\,H_2O\,(l) \longrightarrow MnO_2\,(s) + 3\,Fe^{3+}\,(aq) + 4\,OH^-\,(aq)}} \tag{9}$$

Half-reaction:

– Mn in $\mathrm{MnO_4^-}$: $+7 \to +4$ in $\mathrm{MnO_2}$ $\Leftrightarrow$ gain of **3** electrons. We therefore have a reduction.

Balancing in basic medium:

- On the left, one mole of $\mathrm{MnO_4^-}$ contains 4 oxygen atoms.
- On the right, one mole of $\mathrm{MnO_2}$ contains 2 oxygen atoms.
- To balance oxygen, add 2 molecules of $\mathrm{H_2O}$ on the left.
- This introduces 4 hydrogen atoms on the left, which are balanced by adding 4 $\mathrm{OH^-}$ ions on the right.
- The total charge is balanced: $(-1) + (-3) = -4$ on the left and $4 \times (-1) = -4$ on the right.

The reduction half-equation in basic medium is:

$$\mathrm{MnO_4^- + 2\,H_2O + \mathbf{3}\,e^- \longrightarrow MnO_2 + 4\,OH^-}$$

– Fe: $+2 \to +3$ $\Leftrightarrow$ loss of **1** electron. Iron undergoes oxidation:

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+} + \mathbf{1}\,e^-}$$

Verification:

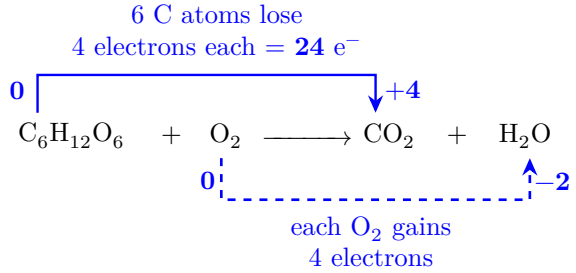
	Left		Right
Mn	1	$\to$	1
Fe	3	$\to$	3
O	$4 + 2 = 6$	$\to$	$2 + 4 = 6$
H	4	$\to$	4
Charge	$-1 + 3(2) = +5$	$\to$	$3(+3) + 4(-1) = +5$

Example 5: Oxidation of glucose Consider a fundamental biological reaction:

$$\mathrm{C_6H_{12}O_6 + O_2 \longrightarrow CO_2 + H_2O} \tag{10}$$

Changes in oxidation numbers:

- **Carbon**: Although the carbon atoms in glucose have different oxidation numbers (ranging from -1 to +1), the **average oxidation number** of carbon is 0. For the overall redox balance, we can consider that each carbon atom goes from an average o.n. of 0 to +4 in $\mathrm{CO_2}$ $\Leftrightarrow$ loss of **4** electrons per C atom.
- **Oxygen** in $\mathrm{O_2}$: $0 \to -2$ in $\mathrm{H_2O}$ and $\mathrm{CO_2}$ (reduction) $\Leftrightarrow$ gain of **2** electrons per O atom.



Electron balance:

- **Oxidation**: 6 C atoms $\times$ 4 electrons/atom = **24 electrons lost**
- **Reduction**: Each $\mathrm{O_2}$ molecule gains 4 electrons (2 O atoms $\times$ 2 $\mathrm{e^-}$/atom)
- To gain 24 electrons, we need $24/4 =$ **6 $\mathbf{O_2}$ molecules**

Overall reaction:

$$\boxed{\mathrm{C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O}} \tag{11}$$

Verification:

	Left		Right
C	6	→	6
H	12	→	12
O	$6 + 12 = 18$	→	$12 + 6 = 18$

In summary, correct assignment of oxidation numbers constitutes a fundamental tool for reading, understanding, and balancing redox reactions.

Application exercises

Exercise 1: Basic oxidation numbers

For each compound, determine the oxidation number of the requested element:
K in K_2O, Cl in HCl, O in Na_2O_2, H in CaH_2, N in NH_3, S in H_2SO_4.

Correction

a) K in K_2O: K is alkali ⇒ $\boxed{+1}$
b) Cl in HCl: H = +1, therefore Cl = $\boxed{-1}$
c) O in Na_2O_2: peroxide ⇒ $\boxed{-1}$
d) H in CaH_2: metal hydride ⇒ $\boxed{-1}$
e) N in NH_3: H = +1, therefore 3(+1) + x = 0 ⇒ x = $\boxed{-3}$
f) S in H_2SO_4: 2(+1) + x + 4(-2) = 0 ⇒ x = $\boxed{+6}$

Exercise 2: Transition metals

Determine the oxidation number of the transition metal in the following compounds:
$FeCl_3$, $KMnO_4$, Cr_2O_3, Cu_2O, $AgNO_3$, $ZnSO_4$.

Correction:

a) $FeCl_3$: 3(-1) + x = 0 ⇒ $\boxed{+3}$
b) $KMnO_4$: K = +1, 4(-2) + 1 + x = 0 ⇒ x = $\boxed{+7}$
c) Cr_2O_3: 3(-2) + 2x = 0 ⇒ x = $\boxed{+3}$
d) Cu_2O: (-2) + 2x = 0 ⇒ x = $\boxed{+1}$
e) $AgNO_3$: NO_3^- = -1, therefore Ag = $\boxed{+1}$
f) $ZnSO_4$: SO_4^{2-} = -2, therefore Zn = $\boxed{+2}$

Exercise 3: Identification of redox reactions

For each equation, indicate whether it is a redox reaction. If so, identify:

- The oxidized element and the reducing agent
- The reduced element and the oxidizing agent

a) $2\,Na(s) + Cl_2(g) \longrightarrow 2\,NaCl(s)$
b) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$
c) $Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$
d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
e) $2\,Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2\,Fe(s)$

Method to follow:
a) Calculate the o.n. of each atom in reactants and products
b) If an atom changes o.n. ⇒ redox reaction
c) O.n. increases ⇒ oxidation ⇒ this atom is the reducing agent
d) O.n. decreases ⇒ reduction ⇒ this atom is in the oxidizing agent

Correction:

a:) $\mathbf{2\,Na\,(s) + Cl_2\,(g) \longrightarrow 2\,NaCl\,(s)}$
- **Oxidation number analysis:**
  - Na(s): 0 → +1 in NaCl (increases by +1)
  - Cl_2(g): 0 → -1 in NaCl (decreases by 1)
- **Conclusion:** This is a redox reaction
- **Identification:**
  - **Oxidized element:** Sodium (Na): 0 → +1
  - **Reducing agent:** Na(s) (it donates electrons)
  - **Reduced element:** Chlorine (Cl): 0 → -1
  - **Oxidizing agent:** Cl_2(g) (it captures electrons)
- **Comment:** This is a typical salt formation reaction by electron transfer.

b:) $\mathbf{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$
- **Oxidation number analysis:**
  - H: +1 in HCl → +1 in H_2O (unchanged)
  - Cl: -1 in HCl → -1 in NaCl (unchanged)
  - Na: +1 in NaOH → +1 in NaCl (unchanged)
  - O: -2 in NaOH → -2 in H_2O (unchanged)
- **Conclusion:** This is NOT a redox reaction
- **Explanation:**
  - No element changes oxidation number
  - This is an acid-base reaction (neutralization)
  - Proton (H^+) exchange, not electrons

c:) $\mathbf{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$
- **Oxidation number analysis:**
  - Zn(s): 0 → +2 in $ZnCl_2$ (increases by +2)
  - H: +1 in HCl → 0 in H_2 (decreases by 1)
  - Cl: -1 in HCl → -1 in $ZnCl_2$ (unchanged)
- **Conclusion:** This is a redox reaction
- **Identification:**
  - **Oxidized element:** Zinc (Zn): 0 → +2
  - **Reducing agent:** Zn(s) (it donates 2 electrons)
  - **Reduced element:** Hydrogen (H): +1 → 0
  - **Oxidizing agent:** HCl (more precisely H^+ in HCl)
- **Comment:** Typical reaction of a metal with an acid, producing a salt and dihydrogen.

d:) $\mathbf{CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g)}$
- **Oxidation number analysis:**
  - Ca: +2 in $CaCO_3$ → +2 in CaO (unchanged)
  - C: +4 in $CaCO_3$ → +4 in CO_2 (unchanged)
  - O: -2 in $CaCO_3$ → -2 in CaO and CO_2 (unchanged)
- **Conclusion:** This is NOT a redox reaction
- **Explanation:**
  - No electron transfer
  - This is thermal decomposition
  - Rearrangement of atoms without change in oxidation state

e:) $\mathbf{2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow Al_2O_3\,(s) + 2\,Fe\,(s)}$
- **Oxidation number analysis:**
  - Al(s): 0 → +3 in Al_2O_3 (increases by +3)
  - Fe: +3 in Fe_2O_3 → 0 in Fe(s) (decreases by 3)

  - O: -2 in Fe_2O_3 → -2 in Al_2O_3 (unchanged)
- **Conclusion:** This is a redox reaction
- **Identification:**
  - **Oxidized element:** Aluminum (Al): 0 → +3
  - **Reducing agent:** Al(s) (strong reducing agent)
  - **Reduced element:** Iron (Fe): +3 → 0
  - **Oxidizing agent:** Fe_2O_3 (iron(III) oxide)
- **Comment:** This is the aluminothermic reaction, used for welding railway tracks.

Method for identifying a redox reaction

How to recognize a redox reaction?:
a) Assign **oxidation numbers** to all atoms
b) Check if there is a **change** for at least one element
c) If yes:
   - **Increase** = oxidation (loss of electrons)
   - **Decrease** = reduction (gain of electrons)
d) Identify:
   - **Reducing agent** = species containing the oxidized element
   - **Oxidizing agent** = species containing the reduced element

Mnemonic: "The reducing agent reduces the other, the oxidizing agent oxidizes the other"

Exercise 4: Balancing simple reactions

Balance the following redox reactions using the oxidation number method:
a) $Mg(s) + O_2(g) \longrightarrow MgO(s)$
b) $Al(s) + HCl(aq) \longrightarrow AlCl_3(aq) + H_2(g)$
c) $Cu(s) + AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + Ag(s)$
d) $Fe_2O_3(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$

Steps to follow for the exercise:
a) Determine the o.n. of all atoms
b) Identify atoms that change o.n.
c) Calculate the number of electrons lost/gained
d) Find the LCM to balance electrons
e) Add stoichiometric coefficients
f) Balance remaining atoms by inspection

Exercise 4: Balancing simple reactions

a) $Mg(s) + O_2(g) \longrightarrow MgO(s)$

Step 1: Determine oxidation numbers
- Mg(s): 0
- $O_2(g)$: 0
- MgO: Mg = +2, O = -2

Step 2: Identify atoms that change
- Mg: 0 → +2 (oxidation, loses 2 e^-)
- O: 0 → -2 (reduction, gains 2 e^- per atom, therefore 4 e^- per O_2 molecule)

Step 3: Balance electrons
- Loss: Mg loses 2 e^-
- Gain: O_2 gains 4 e^-
- LCM = 4

Step 4: Add coefficients

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$$

Verification:

- Mg: 2 atoms on each side.
- O: 2 atoms on each side.

Answer: $2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$

b) $Al(s) + HCl(aq) \longrightarrow AlCl_3(aq) + H_2(g)$

Step 1: Determine oxidation numbers
- Al(s): 0
- HCl: H = +1, Cl = -1
- $AlCl_3$: Al = +3, Cl = -1
- H_2: 0

Step 2: Identify atoms that change
- Al: $0 \rightarrow +3$ (oxidation, loses 3 e^-)
- H: $+1 \rightarrow 0$ (reduction, gains 1 e^- per atom, therefore 2 e^- per H_2 molecule)

Step 3: Balance electrons
- Loss: Al loses 3 e^-
- Gain: $2H^+$ gain 2 e^- (to form H_2)
- LCM = 6

Step 4: Add coefficients
- Multiply Al by 2: 2Al lose 6 e^-
- Multiply HCl by 6: $6\,H^+$ gain 6 e^- (to form $3\,H_2$)

$$2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,AlCl_3(aq) + 3\,H_2(g)$$

Verification:
- Al: 2 atoms.
- Cl: 6 atoms on each side.
- H: 6 atoms on each side.

Answer: $2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,AlCl_3(aq) + 3\,H_2(g)$

c) $Cu(s) + AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + Ag(s)$

Step 1: Determine oxidation numbers
- Cu(s): 0
- $AgNO_3$: Ag = +1, N = +5, O = -2
- $Cu(NO_3)_2$: Cu = +2, N = +5, O = -2
- Ag(s): 0

Step 2: Identify atoms that change
- Cu: $0 \rightarrow +2$ (oxidation, loses 2 e^-)
- Ag: $+1 \rightarrow 0$ (reduction, gains 1 e^-)

Step 3: Balance electrons
- Loss: Cu loses 2 e^-
- Gain: Ag^+ gains 1 e^-
- LCM = 2

Step 4: Add coefficients
- Multiply Ag by 2: $2\,Ag^+$ gain 2 e^-

$$Cu(s) + 2\,AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)$$

Verification:
- Cu: 1 atom.
- Ag: 2 atoms on each side.
- N: 2 atoms on each side.
- O: 6 atoms on each side.

Answer: $Cu(s) + 2\,AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)$

d) $Fe_2O_3(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$

Step 1: Determine oxidation numbers
- Fe_2O_3: Fe = +3, O = -2
- CO: C = +2, O = -2
- Fe(s): 0
- CO_2: C = +4, O = -2

Step 2: Identify atoms that change
- Fe: $+3 \rightarrow 0$ (reduction, gains 3 e^- per atom, therefore 6 e^- for 2 atoms)
- C: $+2 \rightarrow +4$ (oxidation, loses 2 e^-)

Step 3: Balance electrons
- Gain: $2\,Fe_3{}^+$ gain 6 e^-
- Loss: $C_2{}^+$ loses 2 e^-
- LCM = 6

Step 4: Add coefficients
- Multiply CO by 3: $3\,C_2{}^+$ lose 6 e^-

$$Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g)$$

Verification:
- Fe: 2 atoms on each side.
- C: 3 atoms on each side.
- O: 3 + 3 = 6 atoms on each side.

Answer: $Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g)$

Exercise 5: Complex reactions in acidic/basic medium

Balance the following reactions in the indicated medium:

a) **In acidic medium:** $MnO_4{}^-(aq) + Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$
b) **In basic medium:** $Cl_2(g) + OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$
c) **In acidic medium:** $Cr_2O_7{}^{2-}(aq) + C_2H_5OH(aq) \longrightarrow Cr^{3+}(aq) + CO_2(g)$
d) **In basic medium:** $Al(s) + NO_3{}^-(aq) \longrightarrow Al(OH)_4{}^-(aq) + NH_3(aq)$

Advanced techniques for exercise 5:
- **Acidic medium:** Balance O with H_2O and H with H^+
- **Basic medium:**
  a) Balance as in acidic medium
  b) Add OH^- on both sides to neutralize H^+
  c) Simplify $H^+ + OH^- \longrightarrow H_2O$
- For organic compounds, the o.n. of carbon can be calculated as an average

Correction:

a) $MnO_4{}^-(aq) + Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$ in acidic medium

Half-reaction method:
Half-reactions:

$$\text{Oxidation: } Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$\text{Reduction: } MnO_4{}^- \longrightarrow Mn^{2+}$$

Balancing the reduction:
a) O: Add 4 H_2O on the right: $MnO_4{}^- \longrightarrow Mn^{2+} + 4\,H_2O$
b) H: Add 8 H^+ on the left: $8\,H^+ + MnO_4{}^- \longrightarrow Mn^{2+} + 4\,H_2O$
c) Charge: Left = +7, Right = +2, Therefore add 5 e^- on the left

$$8\,H^+ + MnO_4{}^- + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$$

Combination (LCM = 5):
- Oxidation $\times 5$: $5\,Fe^{2+} \longrightarrow 5\,Fe^{3+} + 5\,e^-$
- Addition: $5\,Fe^{2+} + 8\,H^+ + MnO_4{}^- \longrightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$

Answer: $5\,Fe^{2+}(aq) + 8\,H^+(aq) + MnO_4{}^-(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$

b) $Cl_2(g) + OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$ in basic medium

This is a disproportionation: Cl_2 is both oxidized and reduced.
Half-reactions:

$$\text{Reduction: } Cl_2 \longrightarrow 2\,Cl^-$$

$$\text{Oxidation: } Cl_2 \longrightarrow 2\,ClO^-$$

Balancing in basic medium:
For oxidation:

a) Add $2H_2O$ on the right: $Cl_2 + 2\,H_2O \longrightarrow 2\,ClO^-$
b) Add $4H^+$ on the right: $Cl_2 + 2\,H_2O \longrightarrow 2\,ClO^- + 4\,H^+$
c) Add $4e^-$ on the right: $Cl_2 + 2\,H_2O \longrightarrow 2\,ClO^- + 4\,H^+ + 4\,e^-$

For reduction:

$$Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-$$

Combination (LCM = 4):

- Oxidation $\times 1$: $Cl_2 + 2\,H_2O \longrightarrow 2\,ClO^- + 4\,H^+ + 4\,e^-$
- Reduction $\times 2$: $2\,Cl_2 + 4\,e^- \longrightarrow 4\,Cl^-$

$$Cl_2 + 2\,Cl_2 + 2\,H_2O \longrightarrow 2\,ClO^- + 4\,Cl^- + 4\,H^+$$

$$3\,Cl_2 + 2\,H_2O \longrightarrow 2\,ClO^- + 4\,Cl^- + 4\,H^+$$

Conversion to basic medium:

- Add 4 OH^- on both sides
- $4\,H^+ + 4\,OH^- \longrightarrow 4\,H_2O$

$$3\,Cl_2 + 2\,H_2O + 4\,OH^- \longrightarrow 2\,ClO^- + 4\,Cl^- + 4\,H_2O$$

$$3\,Cl_2 + 4\,OH^- \longrightarrow 2\,ClO^- + 4\,Cl^- + 2\,H_2O$$

Answer: $3\,Cl_2(g) + 4\,OH^-(aq) \longrightarrow 2\,ClO^-(aq) + 4\,Cl^-(aq) + 2\,H_2O(l)$

c) $Cr_2O_7{}^{2-}(aq) + C_2H_5OH(aq) \longrightarrow Cr^{3+}(aq) + CO_2(g)$ in acidic medium

This is a titration reaction of ethanol.
Half-reactions:

$$\text{Reduction: } Cr_2O_7{}^{2-} \longrightarrow Cr^{3+}$$

$$\text{Oxidation: } C_2H_5OH \longrightarrow CO_2$$

Balancing the reduction (already seen):

$$14\,H^+ + Cr_2O_7{}^{2-} + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

Balancing the oxidation:

a) Balance C: $C_2H_5OH \longrightarrow 2\,CO_2$
b) Add H_2O to balance O: $C_2H_5OH + 3\,H_2O \longrightarrow 2\,CO_2$
c) Add H^+ to balance H: $C_2H_5OH + 3\,H_2O \longrightarrow 2\,CO_2 + 12\,H^+$
d) Add e^- to balance charge: $C_2H_5OH + 3\,H_2O \longrightarrow 2\,CO_2 + 12\,H^+ + 12\,e^-$

Combination (LCM = 12):

- Oxidation $\times 1$: $C_2H_5OH + 3\,H_2O \longrightarrow 2\,CO_2 + 12\,H^+ + 12\,e^-$
- Reduction $\times 2$: $28\,H^+ + 2\,Cr_2O_7{}^{2-} + 12\,e^- \longrightarrow 4\,Cr^{3+} + 14\,H_2O$

$$C_2H_5OH + 3\,H_2O + 28\,H^+ + 2\,Cr_2O_7{}^{2-} \longrightarrow 2\,CO_2 + 12\,H^+ + 4\,Cr^{3+} + 14\,H_2O$$

Simplification:

$$C_2H_5OH + 16\,H^+ + 2\,Cr_2O_7{}^{2-} \longrightarrow 2\,CO_2 + 4\,Cr^{3+} + 11\,H_2O$$

Answer: $\mathrm{C_2H_5OH(aq) + 16\,H^+(aq) + 2\,Cr_2O_7{}^{2-}(aq) \longrightarrow 2\,CO_2(g) + 4\,Cr^{3+}(aq) + 11\,H_2O(l)}$

d) $\mathrm{Al(s) + NO_3{}^-(aq) \longrightarrow Al(OH)_4{}^-(aq) + NH_3(aq)}$ in basic medium

Half-reactions:

$$\text{Oxidation: } \mathrm{Al \longrightarrow Al(OH)_4{}^-}$$

$$\text{Reduction: } \mathrm{NO_3{}^- \longrightarrow NH_3}$$

Balancing in basic medium:
For oxidation:

a) Add $\mathrm{4OH^-}$ on the left: $\mathrm{Al + 4\,OH^- \longrightarrow Al(OH)_4{}^-}$
b) Add $\mathrm{3\,e^-}$ on the right: $\mathrm{Al + 4\,OH^- \longrightarrow Al(OH)_4{}^- + 3\,e^-}$

For reduction:

a) Add $\mathrm{6H_2O}$ on the left: $\mathrm{NO_3{}^- + 6\,H_2O \longrightarrow NH_3}$
b) Add $\mathrm{9OH^-}$ on the right: $\mathrm{NO_3{}^- + 6\,H_2O \longrightarrow NH_3 + 9\,OH^-}$
c) Add $\mathrm{8\,e^-}$ on the left: $\mathrm{NO_3{}^- + 6\,H_2O + 8\,e^- \longrightarrow NH_3 + 9\,OH^-}$

Combination (LCM = 24):

- Oxidation $\times 8$: $\mathrm{8\,Al + 32\,OH^- \longrightarrow 8\,Al(OH)_4{}^- + 24\,e^-}$
- Reduction $\times 3$: $\mathrm{3\,NO_3{}^- + 18\,H_2O + 24\,e^- \longrightarrow 3\,NH_3 + 27\,OH^-}$

$$\mathrm{8\,Al + 32\,OH^- + 3\,NO_3{}^- + 18\,H_2O \longrightarrow 8\,Al(OH)_4{}^- + 3\,NH_3 + 27\,OH^-}$$

Simplification:

$$\mathrm{8\,Al(s) + 3\,NO_3{}^-(aq) + 18\,H_2O(l) + 5\,OH^-(aq) \longrightarrow 8\,Al(OH)_4{}^-(aq) + 3\,NH_3(aq)}$$

Answer: $\mathrm{8\,Al(s) + 3\,NO_3{}^-(aq) + 18\,H_2O(l) + 5\,OH^-(aq) \longrightarrow 8\,Al(OH)_4{}^-(aq) + 3\,NH_3(aq)}$

Problems:

Problem 1: Oxidation of iron in water

Iron can corrode in the presence of water and oxygen according to the reaction:

$$\mathrm{Fe(s) + O_2(g) + H_2O(l) \longrightarrow Fe_2O_3 \cdot xH_2O(s)} \quad \text{(rust)}$$

a) Balance this reaction for $x = 0$ (formation of $\mathrm{Fe_2O_3}$)
b) Show that the reaction is indeed a redox reaction
c) Calculate the mass of rust ($\mathrm{Fe_2O_3}$) formed from 5.6 g of iron
d) What volume of $\mathrm{O_2}$ (STP) is needed to completely oxidize 10 g of iron?

Problem 2: Disproportionation of chlorine

Chlorine can undergo disproportionation (self-redox) in basic medium:

$$\mathrm{Cl_2(g) + OH^-(aq) \longrightarrow Cl^-(aq) + ClO_3{}^-(aq) + H_2O(l)}$$

a) Balance this reaction
b) Identify the oxidation and reduction half-reactions
c) What is the role of chlorine in this reaction?
d) Calculate the volume of $\mathrm{Cl_2}$ (at 25°C and 1 atm) needed to produce 10 g of $\mathrm{ClO_3{}^-}$

Problem 3: Medical redox titration

In medical analysis, blood glucose is titrated by oxidation with ferricyanide:

$$\mathrm{C_6H_{12}O_6(aq) + [Fe(CN)_6]^{3-}(aq) \longrightarrow C_6H_{10}O_6(aq) + [Fe(CN)_6]^{4-}(aq) + 2\,H^+(aq)}$$

Problem 1: Oxidation of iron in water

1. Balancing for x = 0:

$$\mathrm{Fe(s) + O_2(g) \longrightarrow Fe_2O_3(s)}$$

Oxidation numbers:

- Fe(s): 0
- O_2: 0
- Fe_2O_3: Fe = +3, O = -2

Changes:

- Fe: 0 → +3 (loses 3 e^- per atom, therefore 12 e^- for 4 atoms)
- O: 0 → -2 (gains 2 e^- per atom, therefore 12 e^- for 6 oxygen atoms, i.e., 3 O_2)

LCM = 12:

- Multiply Fe by 4: loses 12 e^-
- Multiply O_2 by 3: gains 12 e^-

$$\boxed{4\,\mathrm{Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)}}$$

Note: Water is the corrosion medium (it facilitates ionic transfers), but it does not appear in this simplified balance for $x = 0$.

2. Why it's a redox reaction:

Iron is oxidized (0 → +3) and oxygen is reduced (0 → -2).

3. Mass of rust formed:

$$M(\mathrm{Fe}) = 55.85 \text{ g/mol}$$

$$M(\mathrm{Fe_2O_3}) = 159.69 \text{ g/mol}$$

$$n(\mathrm{Fe}) = \frac{5.6}{55.85} = 0.100 \text{ mol}$$

From the equation: 4 mol Fe → 2 mol Fe_2O_3

$$n(\mathrm{Fe_2O_3}) = 0.100 \times \frac{2}{4} = 0.050 \text{ mol}$$

$$m(\mathrm{Fe_2O_3}) = 0.050 \times 159.69 = \boxed{7.98 \text{ g}}$$

4. Volume of O_2 needed:

$$n(\mathrm{Fe}) = \frac{10}{55.85} = 0.179 \text{ mol}$$

From the equation: 4 mol Fe → 3 mol O_2

$$n(\mathrm{O_2}) = 0.179 \times \frac{3}{4} = 0.134 \text{ mol}$$

At STP: $V = n \times 22.4$ L/mol

$$V(\mathrm{O_2}) = 0.134 \times 22.4 = \boxed{3.00 \text{ L}}$$

Problem 2: Disproportionation of chlorine

1. Balancing:

$$\mathrm{Cl_2(g) + OH^-(aq) \longrightarrow Cl^-(aq) + ClO_3{}^-(aq) + H_2O(l)}$$

Half-reactions:

$$\text{Reduction: } \mathrm{Cl_2 \longrightarrow 2\,Cl^-}$$

$$\text{Oxidation: } \mathrm{Cl_2 \longrightarrow 2\,ClO_3{}^-}$$

Balancing in basic medium:

- Reduction:

$$\mathrm{Cl_2} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-}$$

- Oxidation (systematic method: balance O with $\mathrm{H_2O}$, H with $\mathrm{OH^-}$, then charge with $\mathrm{e^-}$):

$$\mathrm{Cl_2} \longrightarrow 2\,\mathrm{ClO_3^-}$$

$$\mathrm{Cl_2} + 6\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{ClO_3^-}$$

$$\mathrm{Cl_2} + 6\,\mathrm{H_2O} + 12\,\mathrm{OH^-} \longrightarrow 2\,\mathrm{ClO_3^-} + 6\,\mathrm{H_2O}$$

$$\mathrm{Cl_2} + 12\,\mathrm{OH^-} \longrightarrow 2\,\mathrm{ClO_3^-} + 6\,\mathrm{H_2O} + 10\,\mathrm{e^-}$$

LCM = 10:

- Reduction $\times 5$:

$$5\,\mathrm{Cl_2} + 10\,\mathrm{e^-} \longrightarrow 10\,\mathrm{Cl^-}$$

- Oxidation $\times 1$:

$$\mathrm{Cl_2} + 12\,\mathrm{OH^-} \longrightarrow 2\,\mathrm{ClO_3^-} + 6\,\mathrm{H_2O} + 10\,\mathrm{e^-}$$

$$5\,\mathrm{Cl_2} + \mathrm{Cl_2} + 12\,\mathrm{OH^-} \longrightarrow 10\,\mathrm{Cl^-} + 2\,\mathrm{ClO_3^-} + 6\,\mathrm{H_2O}$$

$$\boxed{3\,\mathrm{Cl_2(g)} + 6\,\mathrm{OH^-(aq)} \longrightarrow 5\,\mathrm{Cl^-(aq)} + \mathrm{ClO_3^-(aq)} + 3\,\mathrm{H_2O(l)}}$$

2. Half-reactions:

- Oxidation:

$$\mathrm{Cl_2} + 12\,\mathrm{OH^-} \longrightarrow 2\,\mathrm{ClO_3^-} + 6\,\mathrm{H_2O} + 10\,\mathrm{e^-}$$

- Reduction:

$$\mathrm{Cl_2} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-}$$

3. Role of chlorine:

Chlorine is both an oxidizing agent (reduced to $\mathrm{Cl^-}$) and a reducing agent (oxidized to $\mathrm{ClO_3^-}$). This is a **disproportionation**.

4. Volume of $\mathrm{Cl_2}$ needed:

$$M(\mathrm{ClO_3^-}) = 35.45 + 3 \times 16.00 = 83.45 \text{ g/mol}$$

$$n(\mathrm{ClO_3^-}) = \frac{10}{83.45} = 0.120 \text{ mol}$$

From the equation: 3 mol $\mathrm{Cl_2}$ → 1 mol $\mathrm{ClO_3^-}$

$$n(\mathrm{Cl_2}) = 0.120 \times 3 = 0.360 \text{ mol}$$

Ideal gas: $V = \dfrac{nRT}{P}$

$$V = \frac{0.360 \times 0.0821 \times 298}{1} = \boxed{8.80 \text{ L}}$$

Problem 3: Medical redox titration – Blood glucose assay

Clinical context

Blood glucose measurement is a fundamental test in medicine, crucial for the diagnosis and monitoring of diabetes. Among the many available methods, the one using ferricyanide as an oxidizing agent is historical, reliable, and still taught for its pedagogical clarity. It perfectly illustrates how a redox reaction can be transformed into a precise diagnostic tool.

Balancing the reaction

The central reaction is the mild oxidation of the aldehyde function of glucose to gluconate (or gluconic acid), coupled with the reduction of ferricyanide to ferrocyanide.

$$C_6H_{12}O_6(aq) + 2\,[Fe(CN)_6]^{3-}(aq) + 2\,OH^-(aq) \longrightarrow C_6H_{12}O_7(aq) + 2\,[Fe(CN)_6]^{4-}(aq) + H_2O\,(l)$$

Half-reactions (basic medium)

- **Oxidation of glucose (aldehyde → carboxylic acid)**:

$$C_6H_{12}O_6 + 2\,OH^- \longrightarrow C_6H_{12}O_7 + H_2O + 2\,e^-$$

- **Reduction of ferricyanide**:

$$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$$

Electron balance and stoichiometry

- Glucose releases 2 electrons.
- Each $[Fe(CN)_6]^{3-}$ ion captures 1 electron.
- Therefore, **2 ferricyanide ions** are needed for 1 glucose.

Verification of atomic and charge balance

- **Atoms**: C (6=6), H (12=12+2-2), O (6+2=7+1), Fe (2=2), CN (12=12).
- **Charges**: Left: $2 \times (-3) + (-2) = -8$; Right: $2 \times (-4) = -8$.

Medical significance and assay principle

This reaction is at the heart of a classic glucose assay method:

- **Principle**: A known volume of ferricyanide solution ($[Fe(CN)_6]^{3-}$) in excess is added to the blood/-plasma.
- **Reaction**: Glucose reduces part of the ferricyanide to ferrocyanide ($[Fe(CN)_6]^{4-}$).
- **Assay**: The remaining excess ferricyanide is then measured (by an adapted titration step).
- **Calculation**: The amount of ferricyanide consumed is proportional to the amount of glucose.

The overall reaction is:

$$\boxed{C_6H_{12}O_6 + 2\,[Fe(CN)_6]^{3-} + 2\,OH^- \longrightarrow C_6H_{12}O_7 + 2\,[Fe(CN)_6]^{4-} + H_2O}$$

Why is this method important?

a) It directly links a complex redox reaction to a concrete medical application.
b) It shows the importance of correct balancing to obtain reliable quantitative results.
c) It illustrates how optical properties (the yellow color of $[Fe(CN)_6]^{3-}$ disappearing upon reduction) can serve as markers in medical analytical chemistry.

The balanced reaction in basic medium is:

$$\boxed{C_6H_{12}O_6 + 4\,[Fe(CN)_6]^{3-} + 4\,OH^- \longrightarrow C_6H_{10}O_6 + 4\,[Fe(CN)_6]^{4-} + 3\,H_2O}$$

This equation faithfully reflects the transfer of 4 electrons from glucose to 4 ferricyanide ions, and constitutes the stoichiometric basis for blood glucose assay by this redox method.

7.3 Half-reaction method for balancing redox equations

7.3.1 Why is it so difficult to balance redox reactions?

Redox reactions are difficult to balance because a valid equation must simultaneously respect: (i) atom conservation and (ii) charge conservation. Let us illustrate this with iron reacting with chlorine.

Observation (laboratory):
Metallic iron reacts with chlorine to form iron(III) and chloride ions.

Direct writing (incorrect):

$$\mathrm{Fe(s) + Cl_2(aq) \longrightarrow Fe^{3+}(aq) + Cl^-(aq)}$$

Intuitive correction (still incorrect):

$$\mathrm{Fe(s) + Cl_2(aq) \longrightarrow Fe^{3+}(aq) + 2\,Cl^-(aq)}$$

	Left side	Right side
Iron atoms	1	1
Chlorine atoms	2	2
Total charge	0	$+3 + 2 \times (-1) = +1$

Problem: atoms are conserved, but **charge is not**. But a redox equation must conserve both **matter** and **charge**.
Correct equation:

$$\mathrm{2\,Fe(s) + 3\,Cl_2(aq) \longrightarrow 2\,Fe^{3+}(aq) + 6\,Cl^-(aq)}$$

	Left side	Right side
Iron atoms	2	2
Chlorine atoms	6	6
Total charge	0	$2 \times (+3) + 6 \times (-1) = 0$

Important

Double condition for a valid redox equation:
a) **Conservation of matter:** same number of atoms of each element.
b) **Conservation of charge:** same total electrical charge.
These two conditions must be verified **simultaneously**.

7.3.2 The need for a systematic method

Balancing "at random" or "by intuition" presents several problems:

- **Waste of time:** You can spend minutes trying different combinations.
- **Frustration:** It is discouraging when you cannot do it.
- **Frequent errors:** Especially for complex reactions involving multiple atoms and/or ionic species.
- **Inaccuracy:** In medicine and biology, precision is crucial.

That is why we will learn the **half-reaction method**: a systematic approach that always yields a correct equation **provided all steps are followed** and that you **verify at the end** the conservation of matter (atoms) and charge.

7.3.3 Key concept: what is a half-reaction?

Definition Half-reaction

A **half-reaction** is the representation of a single one of the two processes that make up a redox reaction:

- Either **oxidation**: loss of electrons
- Or **reduction**: gain of electrons

A half-reaction **never exists alone** in nature, but it is a powerful mathematical tool.

Application to an important medical case: iron assay

In medicine, the concentration of iron in blood often needs to be measured. A classic method uses the reaction with dichromate ion. Here is how to balance this reaction step by step.

Problem statement Consider the reaction in acidic medium:

$$\mathrm{Fe^{2+}(aq) + Cr_2O_7{}^{2-}(aq) \xrightarrow{H^+} Fe^{3+}(aq) + Cr^{3+}(aq)}$$

The mention "H^+" above the arrow is **very important**. It indicates that the reaction occurs in acidic medium, allowing us to use H^+ ions to balance the equation.

Caution

Note on notations:

- Fe^{2+}: iron(II) ion (traditional: ferrous ion).
- Fe^{3+}: iron(III) ion (traditional: ferric ion).
- $Cr_2O_7{}^{2-}$: dichromate ion.
- Cr^{3+}: chromium(III) ion.

In acidic medium, H^+ and H_2O can be used freely.

Step 1: Identify and separate the two half-reactions

Oxidation number analysis:

Element	Initial state	Final state	Conclusion
Iron (Fe)	$+2$ in Fe^{2+}	$+3$ in Fe^{3+}	Oxidation (loss of one electron)
Chromium (Cr)	$+6$ in $Cr_2O_7{}^{2-}$	$+3$ in Cr^{3+}	Reduction (gain of electrons)

We therefore write the crude half-reactions:

$$\text{Oxidation: } Fe^{2+} \longrightarrow Fe^{3+}$$

$$\text{Reduction: } Cr_2O_7{}^{2-} \longrightarrow Cr^{3+}$$

Step 2: Balance atoms other than H and O

- **For iron:** Already balanced (1 atom on each side)
- **For chromium:** Problem! There are 2 chromium atoms on the left (Cr_2) but only 1 on the right

Correction: Put a coefficient 2 in front of Cr^{3+}

$$Cr_2O_7{}^{2-} \longrightarrow 2\,Cr^{3+}$$

Step 3: Balance oxygen with H_2O

Only the chromium reduction contains oxygen. Let us count:

- On the left: 7 oxygen atoms (in Cr_2O_7)
- On the right: 0 oxygen atoms

Rule: Add water molecules (H_2O) to the side that lacks oxygen.
Application: Since 7 O are missing on the right, add 7 H_2O on the right:

$$Cr_2O_7{}^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

Each H_2O brings 1 oxygen atom, so 7 H_2O bring 7 O.

Step 4: Balance hydrogen with H^+

Now, look at the hydrogen introduced by water:

- On the left: 0 hydrogen atoms
- On the right: $7 \times 2 = 14$ hydrogen atoms (in 7 H_2O)

Rule: In acidic medium, use H^+ ions to balance hydrogen.
Application: Add 14 H^+ on the left:

$$14\,H^+ + Cr_2O_7{}^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

Step 5: Balance charge with electrons (crucial step!)

This is the most important and often most delicate step. We must check the total electrical charge on each side.

For iron oxidation:

$$\mathrm{Fe^{2+}} \longrightarrow \mathrm{Fe^{3+}}$$

Charge calculation:

- Left: $+2$
- Right: $+3$
- Difference: $+3 - (+2) = +1$

Rule: Add electrons ($\mathrm{e^-}$) to the more positive side.
Application: Since the right is more positive by 1 unit, add 1 electron on the right:

$$\boxed{\mathrm{Fe^{2+}} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{e^-}}$$

Verification: Left $= +2$, Right $= +3 - 1 = +2$.

For chromium reduction:

$$14\,\mathrm{H^+} + \mathrm{Cr_2O_7^{2-}} \longrightarrow 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O}$$

Detailed charge calculation:

- On the left: $14 \times (+1$ from $\mathrm{H^+}) + (-2$ from $\mathrm{Cr_2O_7^{2-}}) = +14 - 2 = +12$
- On the right: $2 \times (+3$ from $\mathrm{Cr^{3+}}) + 0$ (from $\mathrm{H_2O}$ is neutral) $= +6$
- Difference: $+12 - (+6) = +6$

Application: The left is more positive by 6 units, so add 6 electrons on the left:

$$\boxed{14\,\mathrm{H^+} + \mathrm{Cr_2O_7^{2-}} + 6\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O}}$$

Verification: Left $= +14 - 2 - 6 = +6$, Right $= +6$.

Step 6: Combine the two half-reactions

We now have two perfectly balanced half-reactions:

$$\begin{aligned}\text{Oxidation: } & \mathrm{Fe^{2+}} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{e^-} \\ \text{Reduction: } & 14\,\mathrm{H^+} + \mathrm{Cr_2O_7^{2-}} + 6\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O}\end{aligned}$$

Problem: The number of electrons does not match (1 in oxidation, 6 in reduction).
Solution: Multiply the first equation by 6 to have the same number of electrons:

$$6\,\mathrm{Fe^{2+}} \longrightarrow 6\,\mathrm{Fe^{3+}} + 6\,\mathrm{e^-}$$

Now, add the two equations:

$$\begin{array}{r} 6\,\mathrm{Fe^{2+}} \longrightarrow 6\,\mathrm{Fe^{3+}} + 6\,\mathrm{e^-} \\ 14\,\mathrm{H^+} + \mathrm{Cr_2O_7^{2-}} + 6\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O} \\ \hline 6\,\mathrm{Fe^{2+}} + 14\,\mathrm{H^+} + \mathrm{Cr_2O_7^{2-}} \longrightarrow 6\,\mathrm{Fe^{3+}} + 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O} \end{array}$$

Note: The 6 $\mathrm{e^-}$ cancel out because they appear on both sides.

Final balanced equation

$$\boxed{6\,\mathrm{Fe^{2+}(aq)} + 14\,\mathrm{H^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} \longrightarrow 6\,\mathrm{Fe^{3+}(aq)} + 2\,\mathrm{Cr^{3+}(aq)} + 7\,\mathrm{H_2O\,(l)}}$$

Complete verification:

1. Conservation of matter:

Element	Left	Right
Fe	6	6
Cr	2	2
O	7	7
H	14	14

2. Conservation of charge:
Detailed calculation:

- **Left:** $6 \times (+2) + 14 \times (+1) + 1 \times (-2) = +12 + 14 - 2 = +24$
- **Right:** $6 \times (+3) + 2 \times (+3) + 0 = +18 + 6 = +24$

Conclusion: Both conditions are satisfied. The equation is perfectly balanced!

Methodological summary

The 6 steps to balance a redox equation in acidic medium:

a) **Separate** into oxidation and reduction
b) **Balance atoms** (except H and O)
c) **Balance O** with H_2O
d) **Balance H** with H^+
e) **Balance charge** with e^-
f) **Combine** by equalizing the number of electrons

Mnemonics:

- "O before H": Oxygen first, Hydrogen next
- "Electrons last": Charge is the last thing to balance
- "Always verify both": Atoms AND charge

7.3.4 Why is this method so powerful?

The half-reaction method is not just a calculation technique: it is a reasoning framework. Its power rests on five characteristics that make it a central tool for health sciences:

- **Systematic:** The same procedure applies to all redox reactions. The question "where to start?" disappears: the approach is stable and structures the reasoning.
- **Fail-proof (if the procedure is followed):** By following the steps in order, then **verifying** at the end the conservation of atoms and charge, one obtains a correct overall equation. The result does not depend on "luck," but on a rigorous protocol.
- **Pedagogical:** Each step has chemical meaning: the electron transfer is explicitly tracked, which reinforces understanding and intuition.
- **Adaptable:** Simple or complex reaction, high coefficients, acidic or basic medium: the method remains applicable and provides a unique tool for varied situations.
- **Preparatory:** It introduces the reasoning used in redox titrations and, more broadly, in experimental contexts relevant to biology and laboratory work.

In the following section, the method will be adapted to basic medium. Before that, it is essential to perfectly master the acidic medium case: it is the foundation for the rest.

7.3.5 Application to an important medical case: blood glucose assay

In clinical medicine, precise measurement of blood glucose concentration is a fundamental test for the diagnosis and monitoring of diabetes. Among the many available methods, some exploit redox reactions in basic medium. Let us consider a representative example involving the oxidation of glucose by hypochlorite ion, a reaction that perfectly illustrates the necessary adaptation of the half-reaction method to basic medium.

Clinical problem statement Consider the reaction in basic medium between glucose (simplified here in its aldehyde form $C_6H_{12}O_6$) and hypochlorite ion ClO^-:

$$C_6H_{12}O_6(aq) + ClO^-(aq) \xrightarrow{OH^-} C_6H_{12}O_7(aq) + Cl^-(aq)$$

Glucose is oxidized to gluconic acid $C_6H_{12}O_7$ (the aldehyde becomes a carboxylic acid), while hypochlorite is reduced to chloride.
The mention "OH^-" above the arrow indicates that the reaction takes place in basic medium: during the half-reaction balancing, OH^- and H_2O may be involved, but they can cancel out in the net overall equation.

Caution

Notations and medical context:

- $C_6H_{12}O_6$: Glucose (aldehyde form, reducing agent)
- $C_6H_{12}O_7$: Gluconic acid (carboxylic acid form)
- ClO^-: Hypochlorite ion (oxidizing agent, present in bleach)
- Cl^-: Chloride ion (reduction product)

In basic medium, OH^- and H_2O are preferentially used to balance hydrogen and oxygen atoms (at the half-reaction level).

Step 1: Identify and separate the two half-reactions

Oxidation number analysis:
For glucose, the key change concerns the carbon of the aldehyde function. Formally, it goes from an oxidation number of +1 (in the aldehyde) to +3 (in the carboxylic acid) on the terminal carbon. This represents a loss of 2 electrons per glucose molecule (if considering only this functional carbon).
For hypochlorite, chlorine goes from an oxidation number of +1 in ClO^- to −1 in Cl^-, corresponding to a gain of 2 electrons.

Element/Function	Initial state	Final state	Conclusion
Glucose (C aldehyde)	+1 (approx.)	+3 (in COOH)	Oxidation (loss of 2 e^-)
Chlorine (in ClO^-)	+1	−1 in Cl^-	Reduction (gain of 2 e^-)

We therefore write the crude half-reactions:

$$\boxed{\text{Oxidation: } C_6H_{12}O_6 \longrightarrow C_6H_{12}O_7}$$

$$\boxed{\text{Reduction: } ClO^- \longrightarrow Cl^-}$$

Step 2: Balance atoms other than H and O

- **For glucose:** The carbon chain remains unchanged (6C, 12H). Only one oxygen atom is added.
- **For hypochlorite:** Chlorine is already balanced (1 atom on each side).

Step 3: Balance oxygen with H_2O

- **Oxidation (glucose):** 6 O on the left, 7 O on the right ⇒ add 1 H_2O on the left:

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7$$

- **Reduction (hypochlorite):** 1 O on the left, 0 on the right ⇒ add 1 H_2O on the right:

$$ClO^- \longrightarrow Cl^- + H_2O$$

Step 4: Balance hydrogen with OH^- (specific to basic medium)

- **Oxidation:** in step 3, we have 14 H on the left and 12 H on the right ⇒ add 2 OH^- on the right:

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2\,OH^-$$

- **Reduction:** in step 3, we have 0 H on the left and 2 H on the right ⇒ add 2 OH^- on the left:

$$ClO^- + 2\,OH^- \longrightarrow Cl^- + H_2O$$

Step 5: Balance charge with e^-

For glucose oxidation:

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2\,OH^-$$

Charges: left 0, right −2 ⇒ add 2 electrons on the right:

$$\boxed{C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2\,OH^- + 2\,e^-}$$

For hypochlorite reduction:

$$ClO^- + 2\,OH^- \longrightarrow Cl^- + H_2O$$

Charges: left -3, right $-1 \Rightarrow$ add 2 electrons on the right:

$$\boxed{ClO^- + 2\,OH^- + 2\,e^- \longrightarrow Cl^- + H_2O}$$

Step 6: Combine the two half-reactions

$$\text{Oxidation: } C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2\,OH^- + 2\,e^-$$
$$\text{Reduction: } ClO^- + 2\,OH^- + 2\,e^- \longrightarrow Cl^- + H_2O$$

Observation: The number of electrons matches (2 in each half-reaction). We therefore add directly, then simplify.
Addition:

$$C_6H_{12}O_6 + H_2O + ClO^- + 2\,OH^- + 2\,e^- \longrightarrow C_6H_{12}O_7 + 2\,OH^- + 2\,e^- + Cl^- + H_2O$$

Simplification:

- The 2 e^- cancel out.
- The 2 OH^- cancel out.
- 1 H_2O cancels out (1 on the left, 1 on the right).

Final balanced equation (net overall)

$$\boxed{C_6H_{12}O_6(aq) + ClO^-(aq) \longrightarrow C_6H_{12}O_7(aq) + Cl^-(aq)}$$

Complete verification

1. Conservation of matter:

Element	Left	Right
C	6	6
H	12	12
O	$6 + 1 = 7$	7
Cl	1	1

2. Conservation of charge:

- **Left:** ClO^- has a charge of -1
- **Right:** Cl^- has a charge of -1

Pedagogical explanation

- At the half-reaction level, OH^-, H_2O, and e^- may appear to balance atoms and charges.
- In the net overall equation, these species may cancel out completely: they therefore do not necessarily appear in the global balance.

Chemical significance

Important

Fundamental lesson: In basic medium, the half-reaction method may involve H_2O and OH^-, but the final overall equation must always be validated by:

a) **conservation of matter**;
b) **conservation of charge**.

This reaction illustrates how an oxidizing agent (here ClO^-) can oxidize an aldehyde function to a carboxylic acid function, and why a final systematic verification is essential.

7.3.6 Another application: redox titration of H_2O_2 by MnO_4^- in basic medium:

Hydrogen peroxide H_2O_2 is an **amphoteric** oxidant/reductant in redox: depending on the partner and pH, it can be oxidized to O_2 or reduced to H_2O. Permanganate MnO_4^- is a strong oxidant, but its **reduction products depend strongly on pH**.
Note: In **acidic medium**, MnO_4^- is often reduced to Mn^{2+} (solution). In **basic or neutral medium**, MnO_4^- is typically reduced to $MnO_2(s)$ (brown precipitate). Therefore: **changing the pH changes the overall equation and stoichiometry**.

Statement (basic medium)

We study the redox reaction between MnO_4^- and H_2O_2 in basic medium (presence of OH^-). We expect to observe:

- Progressive disappearance of the purple color of permanganate.
- Possible appearance of a brown precipitate of $MnO_2(s)$.
- Gas evolution of O_2.

Objective Balance the reaction in **basic medium** using the half-equation method.

Step 1: Identify oxidation and reduction (oxidation numbers)

- In MnO_4^-, Mn is in the +VII oxidation state.
- In MnO_2, Mn is at +IV: **reduction** (gain of electrons).
- In H_2O_2, oxygen is at -I; in O_2, it is at 0: **oxidation** (loss of electrons).

Step 2: Write the half-equations in basic medium

(A) Reduction half-equation: $MnO_4^- \longrightarrow MnO_2(s)$ We balance in basic medium using only H_2O and OH^- for H/O.

$$\boxed{MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-}$$

Quick check: O (6=6), H (4=4), charge left $(-1-3) = -4$ and right $(0-4) = -4$.

(B) Oxidation half-equation: $H_2O_2 \longrightarrow O_2$

$$\boxed{H_2O_2 + 2\,OH^- \longrightarrow O_2 + 2\,H_2O + 2\,e^-}$$

Quick check: O (4=4), H (4=4), charge left -2 and right -2.

Step 3: Equalize the number of electrons

LCM(3,2)=6.

- Multiply (A) by 2.
- Multiply (B) by 3.

$$2\,MnO_4^- + 4\,H_2O + 6\,e^- \longrightarrow 2\,MnO_2(s) + 8\,OH^-$$
$$3\,H_2O_2 + 6\,OH^- \longrightarrow 3\,O_2 + 6\,H_2O + 6\,e^-$$

Step 4: Add and simplify

We add, then simplify common species (e^-, OH^-, H_2O):

$$\boxed{2\,MnO_4^-(aq) + 3\,H_2O_2(aq) \longrightarrow 2\,MnO_2(s) + 3\,O_2(g) + 2\,OH^-(aq) + 2\,H_2O(l)}$$

Final verification (very important)

- Mn: 2 on the left, 2 on the right.
- H: $3 \times 2 = 6$ on the left; $2 \times 2 = 4$ (in $2\,H_2O$) + 2 (in $2\,OH^-$) = 6 on the right.
- O: left $2 \times 4 + 3 \times 2 = 14$; right $2 \times 2 + 3 \times 2 + 2 \times 1 + 2 \times 1 = 14$.
- Charge: left $2 \times (-1) = -2$; right $2 \times (-1) = -2$.

Chemical interpretation (what the equation tells us)

- Permanganate (Mn(VII)) is **reduced** to manganese dioxide Mn(IV), a brown solid.
- H_2O_2 is **oxidized** to O_2: gas evolution can therefore be observed.
- The basic medium appears in the equation via OH^- and H_2O (no H^+).

7.3.7 Methodological summary for basic medium

Objective. Balance a redox equation in aqueous **basic** solution while simultaneously respecting:

- **conservation of atoms** (matter);
- **conservation of charge** (global electroneutrality);
- the disappearance of **electrons** e^- from the **global** equation (they are only a calculation tool);
- consistency with the medium: **absence of H^+** in the final equation (basic medium).

Guiding principle (reference method). The most reliable strategy is to first balance each half-equation **as in acidic medium** (using H_2O then H^+), then **convert** to basic medium by eliminating H^+ using OH^-. This approach clearly separates:

- **atomic balancing** (matter);
- **electrical balancing** (charge, via e^-);
- **adaptation to the medium** (basic: OH^- allowed, H^+ forbidden in the final).

The 6 steps (robust and standardizable version).

a) **Separate into two half-equations (oxidation / reduction).**
Isolate the oxidized and reduced parts. Explicitly note:
- **Oxidation:** loss of electrons (production of e^-).
- **Reduction:** gain of electrons (consumption of e^-).

b) **Balance all atoms except H and O.**
Adjust stoichiometric coefficients to conserve each element **other than** H and O.
- **Tip:** preserve groups that remain intact (e.g., SO_4^{2-}, NO_3^-) if relevant.
- **Pitfall:** touching H/O too early often triggers a cascade of errors.

c) **Balance oxygen with H_2O.**
Add H_2O molecules to the side deficient in O atoms, until the number of O is equal.

d) **Balance hydrogen provisionally with H^+.**
Add H^+ ions to the side deficient in H atoms, until the number of H is equal.
Crucial note: the appearance of H^+ at this stage is **normal** and **intermediate**. They will be eliminated in step 6 to obtain a basic medium writing.

e) **Balance charge with electrons e^-.**
Calculate the total charge on each side of the half-equation, then add e^- to the more *positive* side (or less negative) until charges are equal.
- **Instant check:** an oxidation typically places e^- on the right; a reduction typically places them on the left.
- **Pitfall:** do not add e^- before completing atomic balancing (excluding H/O then O then H).

f) **Convert to basic medium, combine, then verify.**
(a) Conversion of each half-equation to basic)
- For each H^+ present, add exactly **one** OH^- **on both sides** of the half-equation.
- Replace each pair $H^+ + OH^-$ by H_2O.
- Then simplify H_2O appearing on both sides (stoichiometric subtraction).

(b) Combination of half-equations)
- Multiply each half-equation by an integer to obtain the **same number** of exchanged electrons.
- **Add** the two half-equations (the e^- must cancel out).
- Simplify, if necessary, any species appearing **on both sides** (often H_2O, sometimes OH^-).

(c) Imperative final verification)
Verify successively, in this order:
- Atoms (including **H** and **O**).
- Total charge.
- Absence of e^- in the global equation.
- Absence of H^+ in the global equation (basic medium).
- Minimal integer coefficients (simplification by a common factor).

Pitfalls specific to basic medium (diagnosis and prevention).

- **OH^- carries both H and O:** using it too early confuses balancing and greatly increases the risk of inconsistencies.
- **Water on both sides:** the presence of H_2O on both sides is not a problem; the error is forgetting to **simplify** them (or simplifying with wrong coefficients).
- **Incomplete neutralization:** if H^+ remains in the final balance, the conversion to basic has not been completed.
- **Forgetting charge:** an equation can conserve atoms but remain wrong if total charge is not conserved.

Mnemonics (reliable, procedure-oriented).

- "**Acid first**, basic next: H_2O then H^+, then OH^- to eliminate H^+."
- "In basic, H^+ is **forbidden at the end**."
- "If O is wrong, look at H_2O; if H is wrong, look at the H^+/OH^- conversion."
- "Verify: atoms → charges → simplifications."

Important

Final message: Balancing in basic medium is not a series of "tricks" but a logical procedure: conserve matter, conserve charge, then impose the constraints of the medium. Systematic verification (atoms, charges, disappearance of e^- and H^+) is an integral part of the scientific rigor expected in biomedical sciences.

7.4 Using redox titrations in analytical chemistry

7.4.1 Introduction to redox titration: from theory to analytical practice

A redox titration is a volumetric assay in which the measured quantity is not a pH, but an *electron transfer* between two redox couples: the species to be titrated (the **analyte**) and the species of known concentration (the **titrant**).In an analytical context, the objective is not only to write a balanced equation: it is to exploit a reproducible redox stoichiometry to relate a volume measurement to an unknown amount of matter.

Definition Redox titration

A **redox titration** is a volumetric assay based on a rapid and quantitative oxidation-reduction reaction between an oxidant and a reductant. At the **equivalence point**, the amounts of matter have been introduced in the proportions imposed by the overall equation, which allows calculating the amount (or concentration) of the analyte.

Why choose a redox titration over an acid-base titration?

- When the species to be titrated does not have an exploitable acid-base behavior (or when the pK_a values do not allow a sharp endpoint).
- When one wants **selectivity** based on a redox potential (a given oxidant can oxidize certain species and not others).
- When instrumental detection of potential (potentiometry) is more robust than pH measurement in a complex medium.
- When the redox indicator (or self-indication) provides a sharp endpoint, even in colored or buffered solutions.

7.4.1.1 Key elements of a successful redox titration

For a redox titration to be analytically exploitable, three requirements dominate:

a) **Unique and constant stoichiometry**: a single main reaction must dominate, with a well-defined overall equation under the operating conditions.
b) **Sufficiently rapid kinetics**: after each addition of titrant, the reaction must be practically complete on the timescale of manipulation.
c) **Reliable detection of the equivalence point**: by color change (indicator) or by instrumental measurement (redox potential, photometry, etc.).

Important

Caution point: a very large equilibrium constant is a *necessary* condition for a so-called "quantitative" titration, but it is not *sufficient* if kinetics are slow or if side reactions consume the titrant.

7.4.1.2 Operational vocabulary (to master absolutely)

- **Equivalence point**: theoretical state where the amounts of oxidant and reductant are exactly in the stoichiometric proportions of the overall equation.
- **Endpoint**: experimental event observed (indicator color change, potential jump, slope break), supposed to coincide as closely as possible with the equivalence point.
- **Indicator error**: difference (in volume) between endpoint and equivalence point, minimized by judicious choice of indicator/method.

7.4.2 Paradigmatic example: titration of Fe^{2+} by permanganate

7.4.2.1 Analytical context

The titration of iron(II) ions by permanganate is a canonical example because it combines:
a) simple stoichiometry,
b) effective visual detection,
c) historical importance (ore analysis) and high pedagogical value.

Chemically, permanganate ion MnO_4^- is a strong oxidant whose reduction products depend on the medium: in acidic medium, it can be reduced to Mn^{2+} (colorless or very faintly colored solution).

7.4.2.2 Reaction fundamentals

The overall transformation is based on the oxidation of iron(II) to iron(III) and the reduction of permanganate:

$$\text{Oxidation: } \boxed{Fe^{2+} \longrightarrow Fe^{3+} + e^-}$$

$$\text{Reduction (acidic medium): } \boxed{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O}$$

Important

Role of acidic medium (conceptual points).

- It provides the H^+ necessary for the permanganate reduction half-reaction.
- It directs manganese toward Mn^{2+} rather than toward $MnO_2(s)$ (brown precipitate) which would make the analysis less clean.
- It limits certain hydrolyses/complexations and helps stabilize dissolved species under reproducible conditions.

7.4.2.3 Overall equation and stoichiometry

After equalizing electrons (multiplying oxidation by 5), we obtain:

$$\boxed{5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O\,(l)}$$

Immediate analytical reading This equation is the "proportionality law" of the titration:

$$n(Fe^{2+}) = 5\,n(MnO_4^-)$$

Thus, one mole of permanganate corresponds to five moles of iron(II) oxidized.

Endpoint detection: self-indication of permanganate

Permanganate has an intense violet coloration. As long as Fe^{2+} ions are present, the added MnO_4^- is consumed and the color disappears. Near the equivalence point, the first trace of excess MnO_4^- gives a persistent pink-violet tint: this is the (practical) **endpoint** of the titration.

7.4.3 Analytical procedure: logic from solid sample to result

7.4.3.1 Typical operational chain (solid sample)

An analysis on ore, tablet, or solid matrix often follows the following sequence:

a) **Dissolution**: transformation of the solid into dissolved species (often by acid attack).
b) **Oxidation state adjustment**: prior conversion of all iron to Fe^{2+} (if necessary), so that the titrated analyte is a single form.
c) **Clarification**: filtration/centrifugation to remove insolubles and excess solid reagents.
d) **Titration**: progressive addition of the titrant $KMnO_4$ under stirring, until the endpoint.
e) **Data processing**: calculation of $n(Fe^{2+})$, then conversion to iron mass and mass percentage if required.

Caution

Major analytical pitfall: incomplete prior reduction.
If a fraction of the iron remains as Fe^{3+} before titration, it is not counted as Fe^{2+} to be oxidized: the volume of permanganate consumed decreases and the iron content is **underestimated**.

7.4.3.2 Calculation relationship at equivalence

Let C_T be the concentration of the titrant MnO_4^- and V_{eq} the volume delivered at equivalence (in L). Then:

$$n(MnO_4^-) = C_T V_{eq} \qquad \Rightarrow \qquad n(Fe^{2+}) = 5\, C_T V_{eq}$$

If the titration is performed on an aliquot V_P of a stock solution of total volume V_{tot}, the total amount of iron(II) in the stock solution is:

$$n_{tot}(Fe^{2+}) = n_P(Fe^{2+})\, \frac{V_{tot}}{V_P}$$

where $n_P(Fe^{2+})$ is the amount of substance titrated in the aliquot.

7.4.3.3 From chemical result to "matter" result

Once $n(Fe)$ is obtained, conversion to mass is direct:

$$m(Fe) = n(Fe)\, M(Fe)$$

and the mass percentage in a sample of mass m_{ech} is:

$$w(Fe) = 100 \times \frac{m(Fe)}{m_{ech}}$$

7.4.4 Critical aspects, error sources, and good practices

7.4.4.1 Chemical factors (selectivity and side reactions)

- **Concomitant reductants/oxidants**: any species capable of reacting with MnO_4^- distorts the measurement (parasitic consumption of titrant).
- **Secondary products**: depending on pH and matrix, manganese can form different species, modifying the apparent stoichiometry.
- **Complexation**: certain ligands can stabilize Fe^{3+} or Fe^{2+} and influence the speed or cleanliness of the endpoint.

7.4.4.2 Experimental factors (volumetric precision)

- **Meniscus reading**: always at eye level; prefer class A burettes in quantitative contexts.

- **Stirring**: essential to avoid local zones of excess titrant that "cheat" the color.
- **Approaching equivalence**: slow the flow drop by drop near the endpoint.

7.4.4.3 Standardization and titrant stability

In practice, a redox titrant must be reliable: known concentration, stable, and if necessary verified by calibration (standardization) on a reference substance. When the titrant solution evolves over time, periodic restandardization is necessary to ensure traceability of results.

7.4.4.4 Examples with solutions:

Example 1: calculating concentration (of a solution):

We titrate $V_P = 25.0$ mL of a solution containing Fe^{2+}. The titrant is $KMnO_4$ of concentration $C_T = 2.00 \cdot 10^{-2}$ mol $\cdot$ L^{-1}. The volume at equivalence is $V_{eq} = 12.5$ mL.

Calculation

$$n(MnO_4^-) = C_T V_{eq} = 2.00 \times 10^{-2} \times 12.5 \times 10^{-3} = 2.50 \times 10^{-4} \text{ mol}$$

$$n(Fe^{2+}) = 5\, n(MnO_4^-) = 1.25 \times 10^{-3} \text{ mol}$$

$$C(Fe^{2+}) = \frac{n(Fe^{2+})}{V_P} = \frac{1.25 \times 10^{-3}}{25.0 \times 10^{-3}} = \boxed{5.00 \times 10^{-2} \text{ mol L}^{-1}}$$

Example 2: mass percentage (solid)

A sample of mass $m_{ech} = 0.500$ g is dissolved and adjusted to Fe^{2+}, then made up to $V_{tot} = 100.0$ mL. We take an aliquot $V_P = 25.0$ mL and titrate: $C_T = 2.00 \cdot 10^{-2}$ mol$\cdot$L^{-1}, $V_{eq} = 12.5$ mL. Take $M(Fe) = 55.85$ g$\cdot$mol^{-1}.

Calculation In the aliquot: $n_P(Fe^{2+}) = 1.25 \times 10^{-3}$ mol (result from Example 1).
In the total solution:

$$n_{tot} = n_P \frac{V_{tot}}{V_P} = 1.25 \times 10^{-3} \times \frac{100.0}{25.0} = 5.00 \times 10^{-3} \text{ mol}$$

$$m(Fe) = n_{tot} M(Fe) = 5.00 \times 10^{-3} \times 55.85 = 2.79 \times 10^{-1} \text{ g}$$

$$w(Fe) = 100 \times \frac{0.279}{0.500} = \boxed{55.8\%}$$

7.4.5 Generalization to other redox systems:

The reasoning to follow during a titration is always the same and proceeds in four steps. First, write the chemical equation of the reaction that occurs and balance it. Then, use the proportion defined by this equation to establish the mathematical relationship that applies at the equivalence point between the titrated reagent and the titrant reagent. Next, use the volume of titrant solution added to calculate the amount of substance it contains. Finally, use this value to determine the quantity you are looking for, such as the concentration of the solution, its purity, or its mass content.
These four steps constitute a universal method applicable to any redox titration. To master this systematic approach, the following exercises propose the complete analysis of different redox systems encountered in clinical and pharmaceutical practice (vitamin C, hydrogen peroxide, thiols).
The detailed solutions, using IUPAC and SI (International System of Units) notations consistent with the course, allow rigorous self-assessment and preparation for continuous assessments.

7.4.6 Exercises and application:

Exercise

We wish to determine the iron content of a siderite ore sample (mainly $FeCO_3$) also containing impurities. For this, we proceed according to the following protocol:

1. We dissolve 1.50 g of the solid sample in concentrated sulfuric acid, causing the reaction:

$$\mathrm{FeCO_3(s) + 2\,H^+(aq) \longrightarrow Fe^{2+}(aq) + CO_2(g) + H_2O\,(l)}$$

   However, partial oxidation by air may also occur, converting some $\mathrm{Fe^{2+}}$ ions to $\mathrm{Fe^{3+}}$.
2. To ensure all iron is in the $\mathrm{Fe^{2+}}$ form before titration, we add an excess of tin(II) chloride solution ($\mathrm{SnCl_2}$), which reduces $\mathrm{Fe^{3+}}$ ions according to:

$$\mathrm{2\,Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow 2\,Fe^{2+}(aq) + Sn^{4+}(aq)}$$

3. The excess $\mathrm{Sn^{2+}}$ is then eliminated by adding mercury(II) chloride ($\mathrm{HgCl_2}$) which gives a white precipitate of $\mathrm{Hg_2Cl_2(s)}$ without oxidizing the $\mathrm{Fe^{2+}}$ ions.
4. The resulting solution is diluted in a 250.0 mL volumetric flask.
5. We take a 20.0 mL aliquot of this solution and titrate it with an acidified potassium permanganate solution ($\mathrm{KMnO_4}$) of concentration $C_r = 0.0250\ \mathrm{mol \cdot L^{-1}}$.

The titration equation is:

$$\mathrm{MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O\,(l)}$$

The measured equivalent volume is $V_{eq} = 10.4$ mL.

a) **Determination of iron(II) concentration**
   (1)- Write the electronic half-equation for the $\mathrm{MnO_4^-/Mn^{2+}}$ couple.
   (2)- Determine the amount of $\mathrm{MnO_4^-}$ that reacted at equivalence.
   (3)- Deduce the amount of $\mathrm{Fe^{2+}}$ present in the 20.0 mL aliquot.
   (4)- Calculate the concentration $C_{\mathrm{Fe^{2+}}}$ of $\mathrm{Fe^{2+}}$ ions in the 250.0 mL flask.

b) **Calculation of iron mass and percentage in the sample**
   (1)- Determine the total amount of iron (in mol) in the 250.0 mL flask, then deduce the mass of iron m_{Fe} present in the initial 1.50 g sample.
   (2)- Calculate the mass percentage of iron $w(\mathrm{Fe})$ in the ore.

c) **Purity analysis and error sources**
   (1)- Assume now that the ore is pure siderite ($\mathrm{FeCO_3}$). Calculate the theoretical mass of iron contained in 1.50 g of pure $\mathrm{FeCO_3}$. Molar masses: $M(\mathrm{Fe}) = 55.85\ \mathrm{g \cdot mol^{-1}}$, $M(\mathrm{FeCO_3}) = 115.86\ \mathrm{g \cdot mol^{-1}}$.
   (2)- Compare with the experimental value found in question 2. Is the result consistent? Propose an explanation if not.
   (3)- The reduction by $\mathrm{SnCl_2}$ is a critical step. What would be the effect on the titration result if:
   - (i) The addition of $\mathrm{SnCl_2}$ was insufficient and $\mathrm{Fe^{3+}}$ ions remained in the solution before titration?
   - (ii) The step of eliminating excess $\mathrm{Sn^{2+}}$ by $\mathrm{HgCl_2}$ was poorly performed and some $\mathrm{Sn^{2+}}$ ions remained in solution?

   Justify the impact on the equivalent volume and on the calculated iron percentage (overestimation or underestimation).

d) **Calculation of siderite mass content**
   (1)- Assuming all iron comes solely from $\mathrm{FeCO_3}$, calculate the mass of siderite corresponding to the amount of iron titrated.
   (2)- Deduce the mass percentage (or content) of $\mathrm{FeCO_3}$ in the ore sample.

Solution: Redox titration of an iron ore

This exercise illustrates a classic analytical method for determining the iron content in an ore. The approach follows a precise experimental protocol that we will analyze step by step. The objective is to understand not only the calculations but also the underlying chemical reasoning.

Overall scheme of the method

a) **Dissolution** of the ore in acid
b) **Reduction** of all iron to $\mathrm{Fe^{2+}}$

c) **Titration** with potassium permanganate
d) **Calculations** of concentration and purity

Solution

Part (a): Determination of iron(II) (Fe_2^{+}) concentration

Question (a.1): Electronic half-equation for the MnO_4^{-}/Mn^{2+} couple

Step-by-step reasoning:

a) Identify oxidation states:
- In MnO_4^{-}: Mn has an o.s. of +7
- In Mn^{2+}: Mn has an o.s. of +2

b) Calculate the change in oxidation state:

$$\Delta o.s. = (+2) - (+7) = -5$$

This means that manganese **gains 5 electrons**.

c) Write the skeleton of the half-equation:

$$MnO_4^{-} \longrightarrow Mn^{2+}$$

d) Balance atoms other than H and O:
- Mn is already balanced (1 atom on each side)

e) Balance oxygen atoms by adding H_2O:
- Left side: 4 O in MnO_4^{-}
- Right side: 0 O
- We add 4 H_2O on the right: $MnO_4^{-} \longrightarrow Mn^{2+} + 4\,H_2O$

f) Balance hydrogen atoms by adding H^{+}:
- Right side: 8 H in 4 H_2O
- Left side: 0 H
- We add 8 H^{+} on the left: $MnO_4^{-} + 8\,H^{+} \longrightarrow Mn^{2+} + 4\,H_2O$

g) Balance electrical charges by adding electrons:
- Left side: -1 (from MnO_4^{-}) + $+8$ (from 8 H^{+}) = $+7$
- Right side: $+2$ (from Mn^{2+}) + 0 (from H_2O) = $+2$
- Charge difference: $+2 - (+7) = -5$
- We therefore add 5 electrons on the left

Final result:

$$\boxed{MnO_4^{-}(aq) + 8\,H^{+}(aq) + 5\,e^{-} \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$$

Interpretation: This half-equation shows that permanganate is a **powerful oxidant** which, in acidic medium, accepts 5 electrons to reduce to manganese(II) ion.

Question (a.2): Amount of MnO_4^{-} at equivalence

Basic formula reminder: For a solution of known concentration, the amount of substance n is calculated by:

$$n = C \times V$$

where:
- n: amount of substance in mol
- C: concentration in $\text{mol} \cdot \text{L}^{-1}$
- V: volume in L

Numerical application:

$$\begin{aligned} n(\mathrm{MnO_4^-}) &= C_r \times V_{eq} \\ &= 0.0250 \text{ mol} \cdot \mathrm{L}^{-1} \times 10.4 \cdot 10^{-3} \text{ L} \\ &= 2.60 \cdot 10^{-4} \text{ mol} \end{aligned}$$

Order of magnitude check:

- $C_r = 0.025$ mol/L: concentration of the titrant reagent (here, potassium permanganate).
- $V_{eq} = 10.4$ mL $= 0.0104$ L: reasonable volume
- Product: $0.025 \times 0.0104 \approx 0.000260$: consistent

$$\boxed{n(\mathrm{MnO_4^-}) = 2.6 \cdot 10^{-4} \text{ mol}}$$

Question (a.3): Amount of Fe^{2+} in the aliquot

Crucial step: Use the stoichiometry of the titration reaction.

Recall of the overall equation:

$$\mathrm{MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O\,(l)}$$

Analysis of stoichiometric coefficients:

- 1 molecule of $\mathrm{MnO_4^-}$ reacts with 5 $\mathrm{Fe^{2+}}$ ions
- Therefore the molar ratio is: $\dfrac{n(\mathrm{Fe^{2+}})}{n(\mathrm{MnO_4^-})} = \dfrac{5}{1} = 5$

Calculation:

$$\begin{aligned} n(\mathrm{Fe^{2+}}) &= 5 \times n(\mathrm{MnO_4^-}) \\ &= 5 \times 2.6 \cdot 10^{-4} \text{ mol} \\ &= 1.3 \cdot 10^{-3} \text{ mol} \end{aligned}$$

$$\boxed{n(\mathrm{Fe^{2+}}) = 1.3 \cdot 10^{-3} \text{ mol}}$$

Therefore: In the 20.0 mL aliquot, there is $1.3 \cdot 10^{-3}$ mol of iron(II) ions.

Question (a.4): Concentration of Fe^{2+} in the 250.0 mL flask

Step 1: Calculate the total amount of Fe^{2+} in the flask The 20.0 mL aliquot represents a fraction of the total solution:

$$\frac{V_{\text{aliquot}}}{V_{\text{flask}}} = \frac{20.0 \text{ mL}}{250.0 \text{ mL}} = \frac{1}{12.5} = 0.08$$

Therefore the total amount in the flask is:

$$\begin{aligned} n_{\text{tot}}(\mathrm{Fe^{2+}}) &= n(\mathrm{Fe^{2+}})_{\text{in 20 mL}} \times \frac{V_{\text{flask}}}{V_{\text{aliquot}}} \\ &= 1.3 \cdot 10^{-3} \text{ mol} \times \frac{250.0 \text{ mL}}{20.0 \text{ mL}} \\ &= 1.3 \cdot 10^{-3} \text{ mol} \times 12.5 \\ &= 1.625 \cdot 10^{-2} \text{ mol} \end{aligned}$$

Step 2: Calculate the concentration The concentration is given by:

$$C = \frac{n}{V}$$

Application:

$$\begin{aligned} C_{\mathrm{Fe}^{2+}} &= \frac{n_{\mathrm{tot}}(\mathrm{Fe}^{2+})}{V_{\mathrm{flask}}} \\ &= \frac{1.625 \cdot 10^{-2}\ \mathrm{mol}}{250.0 \cdot 10^{-3}\ \mathrm{L}} \quad \text{(conversion mL to L)} \\ &= \frac{0.01625\ \mathrm{mol}}{0.2500\ \mathrm{L}} \\ &= 0.065\ \mathrm{mol \cdot L^{-1}} \end{aligned}$$

Significant rounding: The data have 3 significant figures (1.50 g; 0.0250 mol/L; 10.4 mL), therefore:

$$\boxed{C_{\mathrm{Fe}^{2+}} = 0.065\ \mathrm{mol \cdot L^{-1}}}$$

Part (b): Calculation of iron mass and percentage

Question (b.1): Mass of iron in the sample

Reasoning: We have just calculated the total amount of iron in the 250.0 mL flask, which corresponds exactly to the iron present in the 1.50 g of dissolved ore.

Calculation of iron mass:

$$\begin{aligned} m_{\mathrm{Fe}} &= n_{\mathrm{tot}}(\mathrm{Fe}^{2+}) \times M(\mathrm{Fe}) \\ &= 1.625 \cdot 10^{-2}\ \mathrm{mol} \times 55.85\ \mathrm{g \cdot mol^{-1}} \\ &= 0.907\ \mathrm{g} \end{aligned}$$

Check:

- $n_{\mathrm{Fe}} \approx 0.01625$ mol
- $M_{\mathrm{Fe}} \approx 55.85$ g/mol
- Product ≈ 0.907 g: consistent

$$\boxed{m_{\mathrm{Fe}} = 0.907\ \mathrm{g}}$$

Question (b.2): Mass percentage of iron

Definition: The mass percentage represents the mass of iron divided by the total mass of the sample, multiplied by 100.

$$w(\mathrm{Fe}) = \frac{m_{\mathrm{Fe}}}{m_{\mathrm{sample}}} \times 100$$

Application:

$$\begin{aligned} w(\mathrm{Fe}) &= \frac{0.907\ \mathrm{g}}{1.50\ \mathrm{g}} \times 100 \\ &= 0.605 \times 100 \\ &= 60.5\ \% \end{aligned}$$

Note: This result is consistent as it is less than 100%.

$$\boxed{w(\text{Fe}) = 60.5\ \%}$$

Part (c): Purity analysis and error sources

Question (c.1): Theoretical mass of iron in pure $FeCO_3$

Calculation of mass fraction: In pure $FeCO_3$, the mass fraction of iron is:

$$f_{\text{Fe}} = \frac{M(\text{Fe})}{M(\text{FeCO}_3)}$$

Application:

$$\begin{aligned} f_{\text{Fe}} &= \frac{55.85\ \text{g} \cdot \text{mol}^{-1}}{115.86\ \text{g} \cdot \text{mol}^{-1}} \\ &= 0.4819 \quad \text{(i.e., } 48.19\%\text{)} \end{aligned}$$

Mass of iron in 1.50 g of pure $FeCO_3$:

$$\begin{aligned} m_{\text{Fe,theoretical}} &= m_{\text{sample}} \times f_{\text{Fe}} \\ &= 1.50\ \text{g} \times 0.4819 \\ &= 0.7228\ \text{g} \end{aligned}$$

$$\boxed{m_{\text{Fe,theoretical}} = 0.723\ \text{g}}$$

Question (c.2): Comparison and interpretation

Comparison of values:

- Experimental mass: 0.907 g
- Theoretical mass (if pure): 0.723 g
- Ratio: $\dfrac{0.907}{0.723} \approx 1.25$

The experiment gives a value **1.25 times larger** than the theoretical value expected for pure siderite.

Possible explanations:

a) **The ore is not solely composed of siderite**: It may contain other iron-richer compounds (magnetite Fe_3O_4 at 72.4% Fe, hematite Fe_2O_3 at 70% Fe) in addition to $FeCO_3$.

b) **Systematic error in the titration**: For example, excess permanganate added due to poor equivalence point detection.

c) **Chemical interferences**: Other reducing species present in the ore could also react with permanganate.

Conclusion: The analyzed ore is richer in iron than pure siderite, as it probably contains other iron-bearing minerals.

Question (c.3): Error effects in the reduction

(i) Insufficient reduction by $SnCl_2$: If Fe^{3+} ions remain in the solution:

- They do not react with MnO_4^- (the titration only measures Fe^{2+})
- Result: measured $n(Fe^{2+})$ < total $n(\text{Fe})$
- Consequence: **underestimation** of iron content
- Effect on V_{eq}: smaller than the correct value

(ii) Incomplete elimination of Sn^{2+}: If Sn^{2+} ions remain in solution:

- Sn^{2+} is also a reducing agent and reacts with MnO_4^-:

$$2\,MnO_4^- + 5\,Sn^{2+} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,Sn^{4+} + 8\,H_2O$$

- Permanganate oxidizes both Fe^{2+} AND Sn^{2+}
- Result: measured V_{eq} > correct V_{eq} (for Fe^{2+} alone)
- Consequence: **overestimation** of iron content

Part (d) : Calculation of siderite mass content

Question (d.1): Corresponding mass of siderite

Assumption: All titrated iron comes solely from $FeCO_3$.

Calculation of $FeCO_3$ amount:

$$\begin{aligned} n(FeCO_3) &= n_{tot}(Fe^{2+}) \quad \text{(1 Fe atom per FeCO3 molecule)} \\ &= 1.625 \cdot 10^{-2} \text{ mol} \end{aligned}$$

Calculation of mass:

$$\begin{aligned} m(FeCO_3) &= n(FeCO_3) \times M(FeCO_3) \\ &= 1.625 \cdot 10^{-2} \text{ mol} \times 115.86 \text{ g} \cdot \text{mol}^{-1} \\ &= 1.88 \text{ g} \end{aligned}$$

Observation: This mass (1.88 g) is greater than the sample mass (1.50 g)!

$$\boxed{m(FeCO_3) = 1.88 \text{ g} > 1.50 \text{ g}}$$

Question (d.2): Mass percentage of $FeCO_3$

Formal calculation:

$$w(FeCO_3) = \frac{m(FeCO_3)}{m_{sample}} \times 100$$

Application:

$$w(FeCO_3) = \frac{1.88 \text{ g}}{1.50 \text{ g}} \times 100 = 125\ \%$$

Interpretation: This result above 100% confirms that the assumption "all iron comes solely from $FeCO_3$" is false. The ore contains other iron-bearing compounds more concentrated in iron.

Summary of results

Quantity	Value	Comment
$n(MnO_4^-)$	$2.60 \cdot 10^{-4}$ mol	Correct
$n(Fe^{2+})$ in 20 mL	$1.30 \cdot 10^{-3}$ mol	Correct
$C_{Fe^{2+}}$	$0.0650 \text{ mol} \cdot \text{L}^{-1}$	Correct
m_{Fe} experimental	0.907 g	Correct
$w(Fe)$	60.5 %	Consistent
m_{Fe} theoretical (pure)	0.723 g	Reference
$w(FeCO_3)$	125 %	Confirms presence of other minerals

Skills developed

Through this exercise, you have practiced:

a) **Stoichiometric reasoning**: use of coefficients in a balanced equation
b) **Concentration calculations**: $n = C \times V$
c) **Dilution management**: dilution factors
d) **Mass percentage calculations**
e) **Critical analysis of results**: detection of inconsistencies
f) **Identification of error sources**: importance of protocol

Tips for practice

- **Always check** the order of magnitude of results
- **Understand the protocol** before calculating
- **Identify underlying assumptions**
- **Be critical** of improbable results
- **Think about the chemical implications** of potential errors

Exercise

In the pharmaceutical sector, quality control of drugs is essential. We wish to verify the ascorbic acid (vitamin C, $C_6H_8O_6$) content of a tablet sold as a supplement, advertised at 500 mg per tablet. The method used is an indirect titration with iodine (iodometry).

Principle: Ascorbic acid is a reducing agent that reacts rapidly and quantitatively with iodine (I_2) according to the reaction:

$$C_6H_8O_6(aq) + I_2(aq) \longrightarrow C_6H_6O_6(aq) + 2\,H^+(aq) + 2\,I^-(aq)$$

The endpoint is detected by the appearance of the blue color of starch in the presence of excess iodine.

Experimental protocol

1. **Preparation of iodine titrant solution:** Dissolve 6.35 g of solid iodine (I_2) and 20 g of solid potassium iodide (KI) in a little water. Make up to 500.0 mL with distilled water in a volumetric flask. (*Potassium iodide allows solubilization of iodine by forming triiodide ion I_3^-, but for stoichiometry, we consider the equivalent in I_2*).
2. **Preparation of the solution to be titrated:** Finely grind one tablet of total mass $m_{\text{tablet}} = 0.650$ g. Dissolve the powder in acidified water (oxalic acid $H_2C_2O_4$ to stabilize vitamin C). Filter to remove insoluble excipients and make up the filtered solution to 250.0 mL (Solution S).
3. **Titration:** Take $V_P = 20.0$ mL of solution S in an Erlenmeyer flask. Add a few drops of starch indicator. Titrate with the iodine solution. The average equivalent volume obtained from three trials is $V_{eq} = 17.2$ mL.

Data

- Molar mass of ascorbic acid: $M(C_6H_8O_6) = 176.12\ \text{g} \cdot \text{mol}^{-1}$
- Molar mass of iodine: $M(I_2) = 253.8\ \text{g} \cdot \text{mol}^{-1}$
- Oxalic acid ($H_2C_2O_4$) does not interfere with iodine under the titration conditions.

Questions

1) **Study of the titrant solution**
   a) Calculate the theoretical concentration C_T (in $\text{mol} \cdot \text{L}^{-1}$) of the iodine solution prepared in step 1 of the protocol. Assume the weighed mass is exact and dissolution is complete.
   b) Why is potassium iodide (KI) used to prepare this solution?
2) **Stoichiometry of the titration**
   a) Identify the oxidizing agent and the reducing agent in the assay reaction. Justify by recalling the definitions.

b) Write the electronic half-equations for the couples involved:
- Ascorbic acid couple: $C_6H_6O_6$ / $C_6H_8O_6$
- Iodine couple: I_2 / I^-

c) Find the overall equation for the assay reaction. What is the stoichiometric relationship at equivalence between the amounts of iodine and ascorbic acid?

3) **Determination of vitamin C mass in the tablet**

a) Calculate the amount of iodine $n(I_2)_{eq}$ that reacted at equivalence for the 20.0 mL aliquot.

b) Deduce the amount of ascorbic acid n_A present in this aliquot.

c) Calculate the total amount of ascorbic acid n_{tot} in the 250.0 mL flask (solution S).

d) Calculate the corresponding mass of ascorbic acid m_{exp}, expressed in milligrams.

4) **Quality control and interpretation**

a) Calculate the mass percentage (or content) of ascorbic acid in the analyzed tablet.

$$\text{Content} = \frac{m_{\text{exp}}}{m_{\text{tablet}}} \times 100$$

b) The label claims 500 mg of vitamin C per tablet. Is the experimental result compliant? If not, propose two realistic explanations (related to the product or protocol) that could justify the observed discrepancy.

c) Why is oxalic acid added during preparation of solution S? What would be the effect of a basic medium on vitamin C and on the assay result?

5) **Uncertainty analysis and protocol variants**

a) **Sensitivity to air oxidation:** Vitamin C in aqueous solution can be slowly oxidized by dissolved oxygen.
- What would be the effect of too long a waiting time between preparation of solution S and its titration on the determined mass m_{exp}?
- Would this lead to an **overestimation** or **underestimation** of vitamin C content? Justify.

b) **Use of an indicator:** Why is starch used? When is it generally added and why? What would happen if it were added at the very beginning of the titration?

c) **Solubility problem:** The iodine titrant solution is not stable over the long term. For routine quality control, a back-titration method (indirect iodometry) is often used.
- Propose a two-step protocol: (i) Add a known volume in excess of an iodine solution of known concentration to solution S. (ii) Titrate the excess iodine with a sodium thiosulfate solution ($S_2O_3^{2-}$).
- Write the equation for the reaction between thiosulfate and iodine: $I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}$ (tetrathionate).
- Explain how this method can be more accurate for titrating a reducing agent like vitamin C.

Solution

Assay of vitamin C by iodometry

1. Study of the titrant solution

1.a. Theoretical concentration C_T of the iodine solution Data:
- Mass of iodine weighed: $m(I_2) = 6.35$ g
- Molar mass of iodine: $M(I_2) = 253.8\ \text{g} \cdot \text{mol}^{-1}$
- Final volume of solution: $V = 500.0\ \text{mL} = 0.5000\ \text{L}$

Detailed calculation:

a) **Calculation of iodine amount:**

$$n(I_2) = \frac{m(I_2)}{M(I_2)} = \frac{6.35}{253.8}$$

Intermediate calculation:

$$\frac{6.35}{253.8} = \frac{635}{2538} \times 10^{-2} \approx 0.2502 \times 10^{-1} = 0.02502$$

More precisely:

$$\frac{6.35}{253.8} = \frac{6.35 \times 100}{253.8 \times 100} = \frac{635}{25380} = \frac{127}{5076} \approx 0.02502$$

Keeping 3 significant figures:

$$n(\mathrm{I_2}) = 0.0250 \text{ mol}$$

b) **Concentration calculation:**

$$C_T = \frac{n(\mathrm{I_2})}{V} = \frac{0.0250}{0.5000}$$

$$C_T = 0.0500 \text{ mol} \cdot \mathrm{L}^{-1}$$

$$\boxed{C_T = 0.0500 \text{ mol} \cdot \mathrm{L}^{-1}}$$

1.b. Role of potassium iodide KI Iodine ($\mathrm{I_2}$) is sparingly soluble in pure water (solubility ≈ 0.0013 mol/L at 25°C). To increase its solubility and prepare a concentrated solution, potassium iodide is used.
Mechanism:

$$\mathrm{I_2 + I^- \rightleftharpoons I_3^-}$$

- Formation of the **triiodide ion** $\mathrm{I_3^-}$ complex, much more soluble in water
- The reaction is rapid and reversible
- In the presence of vitamin C, $\mathrm{I_2}$ is consumed, shifting the equilibrium to the left
- We can therefore consider that all iodine is available for the reaction

2. Stoichiometry of the titration

2.a. Identification of oxidizing and reducing agents **Definitions:**
- **Oxidizing agent**: chemical species that captures electrons (is reduced)
- **Reducing agent**: chemical species that donates electrons (is oxidized)

Reaction analysis:

$$\mathrm{C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2\,H^+ + 2\,I^-}$$

- **Iodine ($\mathbf{I_2}$)**: goes from oxidation state 0 to -1 (in $\mathrm{I^-}$) → it gains electrons → it is the oxidizing agent
- **Ascorbic acid ($\mathbf{C_6H_8O_6}$)**:
  - Oxidized form: $\mathrm{C_6H_6O_6}$ (dehydroascorbic acid)
  - Reduced form: $\mathrm{C_6H_8O_6}$ (ascorbic acid)
  - Loss of 2H (equivalent to loss of $2e^- + 2H^+$) → it is the reducing agent

$$\boxed{\text{Oxidizing agent: } \mathrm{I_2} \quad \text{Reducing agent: } \mathrm{C_6H_8O_6}}$$

2.b. Electronic half-equations **$\mathbf{I_2/I^-}$ couple:**
- Reduction: $\mathrm{I_2} + 2e^- \rightarrow 2\mathrm{I^-}$

$\mathbf{C_6H_6O_6/C_6H_8O_6}$ couple:
- The conversion of $\mathrm{C_6H_8O_6}$ to $\mathrm{C_6H_6O_6}$ corresponds to oxidation
- We lose 2 H atoms, equivalent to loss of 2 electrons and 2 protons
- Oxidation: $\mathrm{C_6H_8O_6} \rightarrow \mathrm{C_6H_6O_6} + 2H^+ + 2e^-$

$$\boxed{\begin{array}{l}\text{Reduction half-equation: } \mathrm{I_2 + 2\,e^- \longrightarrow 2\,I^-} \\ \text{Oxidation half-equation: } \mathrm{C_6H_8O_6 \longrightarrow C_6H_6O_6 + 2\,H^+ + 2\,e^-}\end{array}}$$

2.c. Overall equation and stoichiometric relationship **Obtaining the overall equation:**

Addition of the two half-equations (electrons cancel out):

$$I_2 + 2\,e^- + C_6H_8O_6 \longrightarrow 2\,I^- + C_6H_6O_6 + 2\,H^+ + 2\,e^-$$

Simplification:

$$\boxed{C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2\,H^+ + 2\,I^-}$$

Stoichiometric relationship:
From the overall equation, the stoichiometric coefficients are 1 for $C_6H_8O_6$ and 1 for I_2.
Therefore at equivalence:

$$\boxed{n_{C_6H_8O_6} = n_{I_2}}$$

1 mole of vitamin C reacts with 1 mole of iodine

3. Determination of vitamin C mass in the tablet

3.a. Amount of iodine at equivalence **Data:**

- Concentration of titrant solution: $C_T = 0.0500 \text{ mol} \cdot \text{L}^{-1}$
- Equivalent volume: $V_{eq} = 17.2 \text{ mL} = 0.0172 \text{ L}$

$$n(I_2)_{eq} = C_T \times V_{eq}$$
$$n(I_2)_{eq} = 0.0500 \times 0.0172$$

Detailed calculation:

$$0.0500 \times 0.0172 = 0.0500 \times (1.72 \times 10^{-2}) = 8.60 \cdot 10^{-4} \text{ mol}$$

$$\boxed{n(I_2)_{\text{eq}} = 8.60 \cdot 10^{-4} \text{ mol}}$$

3.b. Amount of ascorbic acid in the aliquot From the stoichiometric relationship: $n_{C_6H_8O_6} = n_{I_2}$

$$n_A = n(I_2)_{\text{eq}} = 8.60 \cdot 10^{-4} \text{ mol}$$

$$\boxed{n_A = 8.60 \cdot 10^{-4} \text{ mol}}$$

3.c. Total amount in the 250.0 mL flask **Reasoning:**

- The 20.0 mL aliquot represents a fraction of solution S (250.0 mL)
- Dilution factor: $\dfrac{250.0}{20.0} = 12.5$

$$n_{\text{tot}} = n_A \times \frac{V_S}{V_P}$$
$$n_{\text{tot}} = 8.60 \times 10^{-4} \times \frac{250.0}{20.0}$$
$$n_{\text{tot}} = 8.60 \times 10^{-4} \times 12.5$$

Detailed calculation:

$$8.60 \times 10^{-4} \times 12.5 = 8.60 \times 12.5 \times 10^{-4} = 107.5 \times 10^{-4} = 1.075 \times 10^{-2}$$

$$\boxed{n_{\text{tot}} = 1.075 \cdot 10^{-2} \text{ mol}}$$

3.d. Experimental mass of ascorbic acid **Data:** $M(C_6H_8O_6) = 176.12 \text{ g} \cdot \text{mol}^{-1}$

$$m_{\text{exp}} = n_{\text{tot}} \times M(C_6H_8O_6)$$

$$m_{\text{exp}} = 1.075 \times 10^{-2} \times 176.12$$

Detailed step-by-step calculation:

a) $1.075 \times 10^{-2} = 0.01075$

b) $0.01075 \times 176.12 = ?$

Calculation:

$$0.01075 \times 176 = 1.892$$
$$0.01075 \times 0.12 = 0.00129$$
$$\text{Total} = 1.892 + 0.00129 = 1.89329$$

So $m_{\text{exp}} = 1.893$ g

Conversion to milligrams:

$$1.893 \text{ g} = 1893 \text{ mg}$$

$$\boxed{m_{\text{exp}} = 1893 \text{ mg}}$$

4. Quality control and interpretation

4.a. Mass percentage in the tablet **Data:** $m_{\text{tablet}} = 0.650$ g

$$\text{Content} = \frac{m_{\text{exp}}}{m_{\text{tablet}}} \times 100$$
$$\text{Content} = \frac{1.893}{0.650} \times 100$$

Detailed calculation:

$$\frac{1.893}{0.650} = 2.9123...$$
$$2.9123 \times 100 = 291.23$$

$$\boxed{\text{Content} \approx 291\%}$$

4.b. Compliance and explanations **Comparison:**

- Claimed: 500 mg = 0.500 g
- Measured: 1893 mg = 1.893 g

$$\frac{1.893}{0.500} = 3.786 \quad \text{(about 3.8 times more)}$$

Conclusion: The experimental result is **not compliant**.

Two realistic explanations:

a) **Explanation related to the protocol:**
- The iodine solution is not at the theoretical concentration of $0.0500 \text{ mol} \cdot \text{L}^{-1}$
- Possible causes:
  - Weighing error (actual mass of I_2 different from 6.35 g)
  - Impure or partially sublimed iodine
  - Incorrect final volume (volumetric error)

b) **Explanation related to the product:**
- Presence of other reducing substances in the tablet
- Excipients or additives could react with iodine
- Insufficient filtration not removing all interferents

4.c. Role of oxalic acid **Main role:** Stabilize vitamin C by acidifying the medium.
Justification:

- Vitamin C oxidizes slowly in air, especially in neutral or basic medium
- In acidic medium, this oxidation is slowed down
- Oxalic acid is chosen because it does not interfere with iodine

Effect of a basic medium:

a) **On vitamin C:**
   - Accelerated oxidation by atmospheric oxygen
   - Decrease in actual concentration during the assay

b) **On the assay:**
   - Side reaction: $I_2 + 2\,OH^- \longrightarrow I^- + IO^- + H_2O$
   - Formation of hypoiodite (IO^-) which is also an oxidant
   - Additional iodine consumption
   - Biased result (overestimation of vitamin C)

5. Uncertainty analysis and variants

5.a. Sensitivity to air oxidation Effect of too long a waiting time:

- Part of the vitamin C is oxidized by dissolved oxygen
- Less vitamin C remains to be titrated
- The equivalent volume V_{eq} will be smaller

Underestimation of vitamin C mass

Detailed justification:

$$C_6H_8O_6 + \frac{1}{2}\,O_2 \longrightarrow C_6H_6O_6 + H_2O$$

Vitamin C progressively disappears, so $n_{C_6H_8O_6}$ decreases. Since V_{eq} is proportional to $n_{C_6H_8O_6}$, a too small V_{eq} is measured, hence a calculated mass that is too low.

5.b. Use of starch Why use starch?

- Starch forms an intense blue-violet complex with iodine
- Very sensitive: detects traces of iodine ($\approx 10^{-5}$ M)
- Sharp and easy-to-observe color change

Optimal addition time:

- Generally added **near the end of the titration**, when the pale yellow color of iodine becomes very faint
- Justification: If added too early, the starch-I_2 complex can trap iodine and slow down the reaction
- The color change would be less sharp and more gradual

Consequence of addition at the beginning:

- Complex formation from the start
- Slowed reaction (iodine trapped in the complex)
- Gradual color change (blue intensifying)
- Difficulty in precisely identifying the equivalence point

5.c. Back-titration (indirect iodometry) Two-step protocol:

a) **Step 1: Reaction with excess iodine**
   - Take a volume V_S of solution S
   - Add a known volume V_{I_2} of an iodine solution of concentration C_{I_2}
   - This addition must be in large excess relative to vitamin C
   - Allow complete reaction: $C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2\,H^+ + 2\,I^-$

b) **Step 2: Titration of excess iodine**
   - Titrate the excess iodine with a sodium thiosulfate solution $Na_2S_2O_3$ of concentration $C_{S_2O_3^{2-}}$
   - Equation: $I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}$
   - Add starch near the end of the titration

Thiosulfate-iodine equation:

$$\boxed{I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}}$$

Tetrathionate: $S_4O_6^{2-}$ (tetrathionate ion)

Advantages of this method:

a) **Solution stability:**
- Thiosulfate solution is more stable than iodine solution
- A primary standard thiosulfate solution can be prepared

b) **Increased precision:**
- Work by difference (known excess - titrated excess)
- Less sensitive to errors in reading the equivalent volume

c) **Adaptation to slow reactions:**
- Allow time for the vitamin C - iodine reaction to be complete
- No reaction rate problem during titration

d) **Selectivity:**
- Possibility of titrating several reducing agents successively
- Better specificity in complex mixtures

Typical calculation with this method:

$$\begin{aligned} n_{I_2,\text{initial}} &= C_{I_2} \times V_{I_2} \\ n_{I_2,\text{excess}} &= \frac{1}{2} \times C_{S_2O_3^{2-}} \times V_{\text{eq}} \\ n_{I_2,\text{reacted}} &= n_{I_2,\text{initial}} - n_{I_2,\text{excess}} \\ n_{C_6H_8O_6} &= n_{I_2,\text{reacted}} \end{aligned}$$

Redox titration of a hydrogen peroxide-based antiseptic

Exercise

Hydrogen peroxide (H_2O_2) is commonly used as an antiseptic and disinfectant in aqueous solution. As part of quality control, it is necessary to experimentally verify the actual H_2O_2 content of a commercial batch, advertised at 3% (w/V).
The assay is performed by redox titration in acidic medium using a potassium permanganate ($KMnO_4$) solution. An alternative confirmatory method by iodometry will then be discussed.

Chemical and analytical data:
- In acidic medium, permanganate ion MnO_4^- is reduced to Mn^{2+} ion.
- Overall titration reaction (in H_2SO_4 medium):

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O \qquad \text{(a)}$$

- Potassium permanganate is self-indicating: the equivalence point is detected by the appearance of a persistent pale pink coloration.
- Molar masses:
  - $M(H_2O_2) = 34.01\ \text{g} \cdot \text{mol}^{-1}$
  - $M(Na_2C_2O_4) = 134.00\ \text{g} \cdot \text{mol}^{-1}$
- Measured density of the antiseptic solution: $\rho = 1.010\ \text{g} \cdot \text{mL}^{-1}$.

Experimental conditions:
- Concentration of permanganate titrant solution: $C_{MnO_4^-} = 0.020\ \text{mol} \cdot \text{L}^{-1}$
- Volume of antiseptic solution taken: $V_{H_2O_2} = 10.0\ \text{mL}$
- Volume of permanganate added at equivalence: $V_{\text{eq}} = 14.8\ \text{mL}$
- Manufacturer's stated content: « H_2O_2 solution at 3% (w/V) »

Work required

1) **Stoichiometric analysis**
   a) Establish the oxidation and reduction half-equations for the couples involved.
   b) Verify the balancing of the given overall equation.
   c) Deduce the stoichiometric relationship linking the amounts of MnO_4^- and H_2O_2 at equivalence.
2) **Determination of H_2O_2 content**
   a) Calculate the amount of permanganate consumed at equivalence.
   b) Deduce the amount of H_2O_2 contained in the aliquot.
   c) Calculate the molar concentration of H_2O_2 in the antiseptic solution.
   d) Deduce the corresponding mass concentration (in $g \cdot L^{-1}$).
3) **Product compliance check**
   a) Calculate the mass content of the solution as a percentage (w/V).
   b) Compare the obtained value with that indicated on the product label.
   c) Estimate the theoretical density of the solution assuming it contains only water and H_2O_2, then discuss the possible discrepancy with the measured density.
4) **Confirmatory method: iodometric assay**
   a) Write the equation for the reaction between hydrogen peroxide and iodide ion in acidic medium.
   b) Describe the principle and steps of an indirect assay of H_2O_2 by iodometry.
   c) Discuss the analytical interest of this method compared to permanganometry.

Solution

1. Stoichiometric analysis

1.a. Oxidation and reduction half-equations **Couple 1: MnO_4^-/Mn^{2+} (acidic medium)**

Permanganate ion MnO_4^- is the oxidizing agent and is reduced to Mn^{2+} (standard potential $E^\circ = +1.51$ V, source: CRC Handbook).
Reduction half-equation:

$$\boxed{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O}$$

Couple 2: O_2/H_2O_2

Hydrogen peroxide H_2O_2 is the reducing agent and is oxidized to dioxygen ($E^\circ = +0.70$ V).
Oxidation half-equation:

$$\boxed{H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2\,e^-}$$

1.b. Verification of the overall equation The half-equations exchange 5 and 2 electrons respectively. Least common multiple: 10.

Reduction $\times$ 2 :

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

Oxidation $\times$ 5 :

$$5H_2O_2 \rightarrow 5O_2 + 10H^+ + 10e^-$$

Addition and simplification ($16H^+ - 10H^+ = 6H^+$):

$$\boxed{2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O}$$

Balance verified: atoms (Mn, O, H) and charges balanced.

1.c. Stoichiometric relationship at equivalence At equivalence:

$$\frac{n_{\mathrm{MnO_4^-}}}{2} = \frac{n_{\mathrm{H_2O_2}}}{5} \quad \Rightarrow \quad \boxed{n_{\mathrm{H_2O_2}} = \frac{5}{2} n_{\mathrm{MnO_4^-}}}$$

2. Determination of H_2O_2 content

2.a. Amount of permanganate consumed Data: $C_{\mathrm{MnO_4^-}} = 0.0200 \text{ mol} \cdot \text{L}^{-1}$ (3 sig. figs.), $V_{\mathrm{eq}} = 14.8 \text{ mL} = 1.48 \cdot 10^{-2} \text{ L}$.

$$n(\mathrm{MnO_4^-}) = 0.0200 \times 1.48 \times 10^{-2} = 2.96 \cdot 10^{-4} \text{ mol}$$

$$\boxed{n(\mathrm{MnO_4^-}) = 2.96 \cdot 10^{-4} \text{ mol}}$$

2.b. Amount of H_2O_2 in the aliquot

$$n(\mathrm{H_2O_2}) = \frac{5}{2} \times 2.96 \times 10^{-4} = 7.40 \cdot 10^{-4} \text{ mol}$$

$$\boxed{n(\mathrm{H_2O_2}) = 7.40 \cdot 10^{-4} \text{ mol}}$$

2.c. Molar concentration of H_2O_2 $V_{\mathrm{H_2O_2}} = 10.0 \text{ mL} = 1.00 \cdot 10^{-2} \text{ L}$.

$$C(\mathrm{H_2O_2}) = \frac{7.40 \times 10^{-4}}{1.00 \times 10^{-2}} = 0.0740 \text{ mol} \cdot \text{L}^{-1}$$

$$\boxed{C(\mathrm{H_2O_2}) = 0.0740 \text{ mol} \cdot \text{L}^{-1}}$$

2.d. Mass content $M_{\mathrm{H_2O_2}} = 34.01 \text{ g} \cdot \text{mol}^{-1}$ (CRC Handbook).

$$\tau_{\mathrm{H_2O_2}} = 0.0740 \times 34.01 = 2.52 \text{ g} \cdot \text{L}^{-1}$$

$$\boxed{\tau_{\mathrm{H_2O_2}} = 2.52 \text{ g} \cdot \text{L}^{-1}}$$

Interpretation A content of $2.52 \text{ g} \cdot \text{L}^{-1}$ (0.25%) corresponds to a standard "10 volumes" hydrogen peroxide (antiseptic). Labeling consistent.

3. Product compliance check

3.a. Mass content as percentage (w/V) Content (w/V) = mass of solute (g) per 100 mL solution = τ (g/L) / 10.

$$\text{Content (w/V)} = \frac{2.52}{10} = 0.252\,\%$$

$$\boxed{\text{Content} = 0.252\,\%\,(w/V)}$$

3.b. Comparison with label - Claimed: $3\,\%\,(w/V) = 30 \text{ g} \cdot \text{L}^{-1}$ (Eur. Pharm.: specs 2.5-3.5%). - Measured: $2.52 \text{ g} \cdot \text{L}^{-1}$.
Relative deviation:

$$\left(\frac{30.0 - 2.52}{30.0}\right) \times 100 = 91.6\,\%$$

$$\boxed{\text{Relative deviation} = 91.6\,\%}$$

Conclusion: Product **non-compliant** (concentration 12 times lower).

3.c. Theoretical density and discussion Theoretical density (dilute H_2O_2/H_2O solution, $\rho_{\mathrm{H_2O}} = 0.9970 \text{ g} \cdot \text{mL}^{-1}$ at 25°C, CRC):

$$\rho_{\mathrm{theo}} \approx \frac{2.52 + 997.0}{1000} = 0.9995 \text{ g} \cdot \text{mL}^{-1} \approx 1.000 \text{ g} \cdot \text{mL}^{-1}$$

$$\boxed{\rho_{\mathrm{theo}} \approx 1.000 \text{ g} \cdot \text{mL}^{-1}}$$

Measured: $1.010\ \mathrm{g \cdot mL^{-1}}$.
Discussion: Deviation (+1.0%) indicates additives (e.g., stabilizing phosphates, Eur. Pharm. <0038>) increasing ρ.

4. Confirmatory method: iodometric assay

4.a. Reaction between H_2O_2 and I^-

$$\boxed{H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow I_2 + 2\,H_2O}$$

Quantitative with Mo(VI) catalyst.

4.b. Principle of indirect assay Steps:

a) Take/acidify V_{sample}, add excess KI.
b) Allow reaction ($H_2O_2 \rightarrow I_2$).
c) Titration: $I_2 + 2\,{S_2O_3}^{2-} \longrightarrow 2\,I^- + {S_4O_6}^{2-}$ (starch near end).

$$H_2O_2 \equiv 2{S_2O_3}^{2-} \quad \Rightarrow \quad \boxed{n_{H_2O_2} = \frac{1}{2} n_{{S_2O_3}^{2-}}}$$

Permanganometry	**Iodometry**
Advantages: • Rapid (instantaneous) • Self-indicating (violet → colorless) • Official Eur. Pharm. method	**Advantages:** • Very precise (±0.1% possible) • Primary standard ($Na_2S_2O_3$) • Fewer oxidizing interferences
Disadvantages: • Reducing interferences (ascorbate, sugar) • $KMnO_4$ unstable if poorly stored • Over-titration difficult to detect	**Disadvantages:** • Long protocol (2 steps) • Sensitive to O_2/light (I_2 volatile) • H_2O_2/I^- reaction slow without catalyst

4.c. Analytical comparison Iodometry preferred for confirmation (Skoog).

General conclusion

- **Probable causes:**
  - Catalytic decomposition (Fe^{3+}, Mn^{2+} traces): $2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$ ($t_{1/2} < 1$ day)
  - Defective storage: UV light or $T > 30°C$, transparent container
  - Expired or contaminated batch
- **Recommendations:**
  - Immediately reject the analyzed batch
  - Control by iodometry (confirmatory method)
  - Check storage chain (opaque, $< 25°C$)
  - Contact supplier (non-compliance >90%)

$$\boxed{\text{Product NON-COMPLIANT – Actual content: } 0.252\,\% \text{ (vs. } 3\%)}$$

Exercise

Part A — Standardization of $KMnO_4$ (primary standard)

A $KMnO_4$ solution of concentration approximately $0.0200\ \mathrm{mol \cdot L^{-1}}$ is prepared and standardized against sodium oxalate $Na_2C_2O_4$ (pure).

Procedure A

- Weigh $m = 0.1675$ g of $Na_2C_2O_4$ and dissolve in an Erlenmeyer flask.
- Acidify with H_2SO_4 (excess) and heat to 60 °C–70 °C.
- Titrate with $KMnO_4$ until a persistent pink color.
- Volume at equivalence: $V_{\text{eq,A}} = 23.45$ mL.

1) Write the overall equation in acidic medium between MnO_4^- and $C_2O_4^{2-}$.
2) Calculate the exact concentration $C_{MnO_4^-}$ (in $mol \cdot L^{-1}$) of the $KMnO_4$ solution.
3) Give two experimental reasons justifying moderate heating during this standardization.

Exercise

Part B — Assay of the antiseptic by permanganometry

The antiseptic is titrated after dilution. **Procedure B**

- Take $V_0 = 10.00$ mL of antiseptic, then dilute to $V_f = 250.0$ mL in a volumetric flask.
- Take an aliquot $V_a = 25.00$ mL of the diluted solution, acidify (H_2SO_4 in excess), then titrate with $KMnO_4$.
- Equivalence volumes (3 trials): 18.62 mL, 18.55 mL, 18.60 mL.

1) Calculate $V_{eq,B}$ and the maximum deviation.
2) Using the titration equation (equation (a)), determine $n(H_2O_2)$ in the titrated aliquot, then in the flask (250.0 mL), then in the initial 10.00 mL.
3) Deduce the molar concentration C_0 of H_2O_2 in the original antiseptic.
4) Convert C_0 to mass content:
   - in % w/V (g of H_2O_2 per 100 mL of antiseptic),
   - then in % w/w using $\rho = 1.010$ g $\cdot$ mL^{-1}.
5) Cite three sources of errors/biases specific to this redox assay and indicate the probable direction (overestimation / underestimation).

Exercise

Part C — Iodometric confirmation (interference discussion)

It is suspected that a reducing compound is present in the matrix (oxidizable stabilizer) that could also consume MnO_4^- in acidic medium, thus skewing the permanganometric assay.
To confirm and correct this interference, an iodometric assay of H_2O_2 is performed in the same matrix.

Iodometry reminders

$$H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow I_2 + 2\,H_2O \quad (1)$$

$$I_2 + 2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2\,I^- \quad (2)$$

1) Explain qualitatively why a parasitic reducing agent causes a positive interference (overestimation of the content) in permanganometry.
2) Propose an iodometric strategy (with a blank test) to correct the matrix effect.
3) From the above equations, establish the stoichiometric relationship between $n(H_2O_2)$ and $n(S_2O_3^{2-})$ at equivalence.

Exercise

Part D — Synthesis and validation

1) The manufacturer claims a concentration of 3.0 % (w/w) of H_2O_2. Is the result obtained in part B compliant with specifications?
2) In case of non-compliance, which method (permanganometry or iodometry) would be most reliable to decide? Justify.
3) Why is standardization of $KMnO_4$ necessary before the assay, even though its concentration is prepared theoretically?

Detailed correction

Solution

Part A — Standardization

1) - Overall equation $\mathbf{MnO_4^-/C_2O_4^{2-}}$ Half-equations in acidic medium:

$$\mathrm{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O}$$
$$\mathrm{C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-}$$

LCM of electrons = 10, hence:

$$\mathrm{2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O.}$$

2)- Calculation of $C_{\mathrm{MnO_4^-}}$

$$n(\mathrm{Na_2C_2O_4}) = \frac{m}{M} = \frac{0.1675\ \mathrm{g}}{134.00\ \mathrm{g\cdot mol^{-1}}} = 1.250\cdot 10^{-3}\ \mathrm{mol}.$$

In the Erlenmeyer: $n(\mathrm{C_2O_4^{2-}}) = 1.250\cdot 10^{-3}$ mol.
Stoichiometry gives:

$$n(\mathrm{MnO_4^-}) = \frac{2}{5}\,n(\mathrm{C_2O_4^{2-}}) = \frac{2}{5}\times 1.250\cdot 10^{-3}\ \mathrm{mol} = 5.00\cdot 10^{-4}\ \mathrm{mol}.$$

Since $V_{\mathrm{eq,A}} = 23.45\ \mathrm{mL} = 2.345\cdot 10^{-2}$ L, therefore:

$$C_{\mathrm{MnO_4^-}} = \frac{n}{V} = \frac{5.00\cdot 10^{-4}\ \mathrm{mol}}{2.345\cdot 10^{-2}\ \mathrm{L}} = 2.132\cdot 10^{-2}\ \mathrm{mol\cdot L^{-1}}.$$

3)- Why heat?

- At room temperature, the oxidation of $\mathrm{C_2O_4^{2-}}$ by $\mathrm{MnO_4^-}$ is slow: heating improves kinetics and avoids a false equivalence (too long waiting, reading drift).
- The reaction is favored once a small amount of $\mathrm{Mn^{2+}}$ is formed (auto-acceleration effect): heating helps to quickly reach a net and reproducible reaction regime.

Solution

Part B — Assay of $\mathbf{H_2O_2}$
1)- Average and precision

$$V_{\mathrm{eq,B}} = \frac{18.62 + 18.55 + 18.60}{3} = 18.59\ \mathrm{mL}.$$

Maximum deviation:

$$\Delta V_{\max} = 18.62 - 18.55 = 0.07\ \mathrm{mL}.$$

2)- Amounts of substance via the titration equation At equivalence, from equation (a):

$$\frac{n(\mathrm{H_2O_2})}{n(\mathrm{MnO_4^-})} = \frac{5}{2} \quad\Rightarrow\quad n(\mathrm{H_2O_2}) = \frac{5}{2}\,n(\mathrm{MnO_4^-}).$$

Moles of permanganate added to the aliquot:

$$n(\mathrm{MnO_4^-}) = C_{\mathrm{MnO_4^-}}\,\overline{V}_{\mathrm{eq,B}} = 2.132\cdot 10^{-2}\ \mathrm{mol\cdot L^{-1}}\times 18.59\cdot 10^{-3}\ \mathrm{L} = 3.963\cdot 10^{-4}\ \mathrm{mol}.$$

Therefore, in the aliquot (25.00 mL of diluted solution):

$$n_a(\mathrm{H_2O_2}) = \frac{5}{2}\times 3.963\cdot 10^{-4}\ \mathrm{mol} = 9.907\cdot 10^{-4}\ \mathrm{mol}.$$

In the flask (250.0 mL), factor 250.0/25.00 = 10:

$$n_f(\mathrm{H_2O_2}) = 10\,n_a(\mathrm{H_2O_2}) = 9.907\cdot 10^{-3}\ \mathrm{mol}.$$

These moles correspond to the initial 10.00 mL:

$$n_0(\mathrm{H_2O_2}) = 9.907 \cdot 10^{-3}\ \text{mol}.$$

3)- Molar concentration in the original antiseptic

$$C_0 = \frac{n_0}{V_0} = \frac{9.907 \cdot 10^{-3}\ \text{mol}}{10.00 \cdot 10^{-3}\ \text{L}} = 0.9907\ \text{mol} \cdot \text{L}^{-1}.$$

4)- Conversion to % w/V then % w/w Mass of $\mathrm{H_2O_2}$ per liter:

$$\gamma_m = C_0\, M(\mathrm{H_2O_2}) = 0.9907\ \text{mol} \cdot \text{L}^{-1} \times 34.01\ \text{g} \cdot \text{mol}^{-1} = 33.69\ \text{g} \cdot \text{L}^{-1}.$$

Therefore, per 100 mL:

$$33.69\ \text{g} \cdot \text{L}^{-1} \times 0.100\ \text{L} = 3.369\ \text{g}.$$

Thus, % w/V content:

$$\boxed{\mathrm{H_2O_2} = 3.37\ \text{g per 100 mL} \quad \Rightarrow \quad 3.37\ \%\ (w/V).}$$

For % w/w: mass of 100 mL of antiseptic:

$$m_{\text{solution}} = \rho\, V = 1.010\ \text{g} \cdot \text{mL}^{-1} \times 100\ \text{mL} = 101.0\ \text{g}.$$

Therefore:

$$w(\mathrm{H_2O_2}) = \frac{3.369\ \text{g}}{101.0\ \text{g}} \times 100 = 3.33\ \%\ (w/w).$$

5)- Errors and biases (expected direction)

- Overshooting the endpoint (too persistent pink) ⇒ volume too large ⇒ $n(\mathrm{MnO_4^-})$ overestimated ⇒ $\mathrm{H_2O_2}$ overestimated.
- Presence of a reducing agent in the matrix also consuming $\mathrm{MnO_4^-}$ (positive interference in acidic medium) ⇒ $\mathrm{H_2O_2}$ overestimated.
- Prior decomposition of $\mathrm{H_2O_2}$ (light, metal traces, storage) before titration ⇒ $\mathrm{H_2O_2}$ underestimated.

Solution

Part C — Iodometry and blank

1)- Why positive bias in permanganometry? Any reducing species oxidizable by $\mathrm{KMnO_4}$ in acidic medium consumes part of the titrant, increasing the volume at equivalence and simulating a higher amount of $\mathrm{H_2O_2}$ (positive interference).

2)- Iodometric strategy with blank

- Add a known excess of $\mathrm{I^-}$ in acidic medium: $\mathrm{H_2O_2}$ releases $\mathrm{I_2}$ according to equation (1).
- Titrate the $\mathrm{I_2}$ formed with $\mathrm{S_2O_3^{2-}}$ according to equation (2) (starch near equivalence).
- Perform a **matrix blank** (same reagents, same procedure, but without $\mathrm{H_2O_2}$ or with $\mathrm{H_2O_2}$ destroyed) to quantify iodine release/consumption due solely to the matrix, then correct the result.

3)- Stoichiometric link $n(\mathrm{H_2O_2})$ / $n(\mathrm{S_2O_3^{2-}})$ From equation (1): 1 mole of $\mathrm{H_2O_2}$ produces 1 mole of $\mathrm{I_2}$.
From equation (2): 1 mole of $\mathrm{I_2}$ consumes 2 moles of $\mathrm{S_2O_3^{2-}}$.
Therefore:

$$n(\mathrm{S_2O_3^{2-}}) = 2\, n(\mathrm{I_2}) = 2\, n(\mathrm{H_2O_2}) \quad \Rightarrow \quad \boxed{n(\mathrm{H_2O_2}) = \frac{1}{2}\, n(\mathrm{S_2O_3^{2-}}).}$$

Solution

Part D — Synthesis and validation

1)- Compliance with specifications The obtained result is 3.33 % (w/w), while the claim is 3.0 %

(w/w).

- The deviation is +0.33 percentage points.
- In the pharmaceutical field, the tolerance is generally ±5% to ±10% on the active ingredient.
- Here, the relative deviation is about +11%, which could be considered non-compliant according to laboratory criteria.

2)- Comparison of methods In case of doubt, the iodometric method would be more reliable because:

- It is more specific to H_2O_2 (reduction of I_2 by other reducing agents is less likely than with MnO_4^-).
- The possibility of a matrix blank allows correction of interferences.
- Detection with starch is very sensitive and precise.

Permanganometry remains faster and simpler, but more subject to interferences.

3)- Necessity of standardization Standardization of $KMnO_4$ is essential because:

- $KMnO_4$ is not a primary standard: it may contain impurities (manganese dioxide MnO_2) and slowly decompose in water.
- Its concentration changes over time (oxidation of water, light, temperature).
- For quantitative quality control analysis, precision of titrant concentration is critical.
- Sodium oxalate ($Na_2C_2O_4$) is an excellent primary standard: pure, stable, precise molar mass.

Transition

Transition: From chemical transformation to physical measurement

In the previous chapter, redox was studied as a **chemical transformation** based on electron exchanges: identification of oxidizing/reducing couples, calculation of oxidation numbers, and especially writing in half-equations to obtain a rigorous overall balance. This step is essential, as it gives the universal language of redox: a reaction is understood by **who** donates electrons, **who** captures them, and **how many** electrons are actually exchanged.
However, a deeper question naturally arises: how to **quantify the "strength"** of a redox couple, that is, its tendency to oxidize or reduce, without limiting oneself to qualitative comparisons? In other words, can a **measurable quantity** be associated with a redox system, summarizing the state of the medium and allowing prediction of the direction of evolution when concentrations (or pH) change?

The fundamental idea of electrochemistry

This is precisely the subject of **electrochemistry**: linking electron transfer chemistry to a physical quantity, the *potential*, measurable using electrodes and an electrochemical cell.
The central idea is to *separate* the two half-reactions at two electrodes:

- Oxidation occurs at the **anode** (negative pole),
- Reduction occurs at the **cathode** (positive pole),
- Electrons then flow through an **external circuit**.

Under these conditions, the reaction manifests not only as a change in composition (as in homogeneous solution), but also as an **electrical potential difference** between the two electrodes.

The Nernst equation: the bridge between chemistry and physics

At equilibrium (open circuit), this potential difference depends on the composition of the medium via the **Nernst equation**, which relates the potential to the reaction quotient and allows, in particular, bridging:

- Standard potentials of couples,
- Equilibrium constants of reactions,
- Non-standard conditions (variable concentrations, pH influence).

From qualitative prediction to quantitative analysis

Thus, this new chapter does not replace the redox chapter: it *organizes* it around an experimental measurement and analytical and biomedical applications:

- **Potentiometry** (titrations, selective electrodes),

- **Biomedical sensors** (glucometers, pO_2 measurement),
- **Control** of oxidizing/reducing media (disinfection, corrosion).

The redox couples and electron balances introduced earlier then become predictive tools: we no longer ask only "**which reaction is possible?**", but also "**what voltage results from it, and how does this voltage vary with the medium?**"

This chapter gives you the keys to transform a chemical reaction into a measurable and usable signal.

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