University of Mohamed Khider – Biskra
Faculty of Exact Sciences
Department of Materials Science

Academic Year: 2025/2026
First Year – Professional Physics
Chemical Analysis Methods

First Semester Examination

Exercise 1: (8 points)

Answer **True or False**, and correct the statement if it is false.

1. The molar concentration of the acid H_3PO_4 is 1.0 mol/L if its normality is 2.0 N.
2. In a sulfuric acid solution H_2SO_4 with a concentration of 0.5 mol/L, the concentration of hydrogen ions H^+ is equal to 1.0 mol/L.
3. When titrating a strong acid with a strong base, the medium is a buffer solution at the equivalence point.
4. A complex is formed of a central atom and ligands connected by coordinate bonds.
5. The secondary valency of a complex determines its geometric shape.
6. The primary valency of a complex is related to the ligands.
7. If the concentration of $KMnO_4$ is 0.02 mol/L, then its normality has the same value.
8. The oxidation number of manganese Mn in the compound $KMnO_4$ is 7.
9. In the two redox couples
   $KMnO_4 / Mn^{2+}$ ($E° = +1.51$ V) and $H_2C_2O_4 / CO_2$ ($E° = -0.49$ V), oxalic acid $H_2C_2O_4$ is the oxidizing agent.
10. In the salt $K_2Cr_2O_7$, the concentration of K^+ ions is equal to the solubility of the salt.

Exercise 2: (6 points)

We want to determine the total hardness of mineral water by a complexometric titration using EDTA, represented by the formula Y^{4-}.

A sample of this water with a volume of 100 mL was taken and titrated with an EDTA solution of concentration 0.01 mol/L.
The volume of EDTA solution consumed at the equivalence point was 15 mL.

Water hardness is due to the presence of calcium ions Ca^{2+} and magnesium ions Mg^{2+}.

The bottle label indicates that the mass concentration of calcium ions is 80 mg/L, and that of magnesium ions is 24 mg/L.

We know that the molar mass of calcium is 40 g/mol and that of magnesium is 24 g/mol.

Questions:

1. Write the equations for the formation of complexes between calcium ions, magnesium ions, and EDTA.

2. Calculate the amount of substance of EDTA used at the equivalence point.
3. Deduce the amount of substance of total hardness ions in the water sample.
4. Calculate the total hardness concentration in mol/L.
5. Express the hardness in hydrotimetric degrees (°TH).
6. Based on the mass concentrations given on the bottle, calculate the theoretical total hardness and comment on the difference between the two values.

Exercise 3: (6 points)

We carry out a titration of a strong acid solution (HCl) with a weak base solution (NH_3) and study the variation of pH during the titration.

The chemical reaction equation is:

$$\mathrm{H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O}$$

Data:

$V_A = 20$ mL, $C_A = 0.01$ mol/L, $C_B = 0.01$ mol/L, $K_a(\mathrm{NH_4^+/NH_3}) = 5.6 \times 10^{-10}$

Complete the titration stages table and calculate the pH.

Stage	Volume of base added (V^B)	Chemical state of the mixture	pH expression	pH value
1	0			
2	10			
3	(V_E = ?)			
4	30			

Answers and Corrections for Exercise 1:

1. False.
Correction: H_3PO_4 is a triprotic acid, meaning it can donate 3 H^+ ions. The relationship is: **Normality (N) = Molarity (M) × n** (where *n* is the number of exchangeable H^+ ions per molecule).
Given Normality = 2.0 N, the Molarity = N / n = 2.0 / 3 ≈ **0.67 mol/L**.

2. True.
H_2SO_4 is a strong diprotic acid and dissociates completely: $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$. Therefore, $[H^+] = 2 \times [H_2SO_4] = 2 \times 0.5 =$ **1.0 mol/L**.

3. False.
Correction: At the equivalence point in a strong acid-strong base titration, the solution contains only a neutral salt and water, resulting in a pH of 7. There is **no buffer** system present.

4. True.
This is the definition of a coordination complex. The central atom (often a metal ion) accepts electron pairs from ligands via coordinate (dative covalent) bonds.

5. True.
The secondary valency (coordination number) dictates how many ligands can attach and thus determines the complex's **geometry** (e.g., octahedral for CN=6, tetrahedral for CN=4).

6. False.
Correction: The primary valency corresponds to the **oxidation state** of the central metal ion. It is satisfied by **counter-ions** (not directly by ligands in the coordination sphere). Ligands satisfy the secondary valency.

7. False.
Correction: $KMnO_4$ acts as a strong oxidizing agent in acidic medium, where Mn goes from +7 to +2. This involves a gain of **5 electrons**. Therefore, Normality = Molarity × 5 = 0.02 × 5 = **0.10 N**.

8. True.
Let the oxidation number of Mn be *x*.
For $KMnO_4$: (+1 from K) + (*x* from Mn) + 4×(-2 from O) = 0 → 1 + x - 8 = 0 → x = **+7**.

9. False.
Correction: The species with the **higher** standard reduction potential (E°) is the stronger oxidizing agent.
Here, $E°(MnO_4^-/Mn^{2+}) = +1.51$ V > $E°(H_2C_2O_4/CO_2) = -0.49$ V. Therefore, **$KMnO_4$** is the oxidizing agent, and **oxalic acid ($H_2C_2O_4$)** acts as the reducing agent.

10. False.

Correction: $K_2Cr_2O_7$ dissociates in water: $K_2Cr_2O_7(s) \rightarrow 2K^+(aq) + Cr_2O_7^{2-}(aq)$. If the solubility (molar concentration of the dissolved salt) is **S mol/L**, then $[K^+]$ = **2S mol/L**. Therefore, $[K^+]$ is **twice** the solubility, not equal to it.

Exercise 2 Solution: Determination of Water Hardness

1. Complex Formation Equations with EDTA (Y^{4-})

The reactions show a 1:1 complex formation for both divalent cations.

- $\mathbf{Ca^{2+}(aq) + Y^{4-}(aq) \rightarrow CaY^{2-}(aq)}$
- $\mathbf{Mg^{2+}(aq) + Y^{4-}(aq) \rightarrow MgY^{2-}(aq)}$

2. Amount of EDTA Used at Equivalence Point

- Given:
    - C(EDTA) = 0.01 mol/L = 1.0×10^{-2} mol/L
    - V(EDTA) = 15 mL = 1.5×10^{-2} L
- Formula: n = C × V
- Calculation:
  n(EDTA) = (1.0×10^{-2} mol/L) × (1.5×10^{-2} L) = 1.5×10^{-4} mol

3. Amount of Total Hardness Ions ($Ca^{2+} + Mg^{2+}$)

Since both ions react in a 1:1 molar ratio with EDTA, n(total ions) = n(EDTA) = 1.5×10^{-4} mol

4. Total Hardness Concentration

- Given: Volume of water sample, V(water) = 100 mL = 0.100 L
- Formula: C = n / V
- Calculation:
  C(total hardness) = (1.5×10^{-4} mol) / (0.100 L) = 1.5×10^{-3} mol/L

$$1^\circ f = 1.0 \times 10 \ \mathrm{m}mol/L$$

$$TH = \frac{1.5 \times 10^{-3}}{1.0 \times 10^{-4}} = 15^\circ f$$

6) Calculating Theoretical Hardness Based on the Bottle

Converting mass concentrations to molarity

- Calcium:
  38.5 mg/L = 0.0385 g/L
  C_Ca^{2+} = 0.0385 / 40 = 9.63×10^{-4} mol/L

- Magnesium:
  7 mg/L = 0.007 g/L
  C_Mg^{2+} = 0.007 / 24 = 2.9×10^{-4} mol/L

Theoretical total hardness

C_TH, theoretical = C_Ca^{2+} + C_Mg^{2+}
C_TH, theoretical ≈ 1.253×10^{-3} mol/L

TH_theoretical = 1.253 × 10 = 12.53 °f

Exercise 3: Titration of a Strong Acid (HCl) with a Weak Base (NH_3)

Given:

- *Volume of acid,* $V_A = 20\ mL$
- *Concentration of acid,* $C_A = 0.01\ mol/L$
- *Concentration of base,* $C_B = 0.01\ mol/L$
- *Acid dissociation constant of ammonium ion,* $K_a(NH_4^+/NH_3) = 5.6 \times 10^{-10}$

Equivalence point volume:

$$V_E = \frac{C_A V_A}{C_B} = \frac{0.01 \times 20}{0.01} = 20\ mL$$

The table below summarizes the titration stages and pH calculations.

Stage	*Volume of base added (mL)*	*Chemical state of the mixture*	*pH expression*	*pH value*
1	*0*	*Strong acid solution (HCl)*	$pH = -log\ (C_A)$	*2.00*
2	*10*	*Excess strong acid and ammonium ions*	$[H^+] = \frac{C_A V_A - C_B V_B}{V_A + V_B}$ $pH = -log\ [H^+]$	*2.48*

3	*20 (equivalence)*	*Ammonium ions (weak acid)*	$[H^+] = \sqrt{K_a \cdot [NH_4^+]}$ $[NH_4^+] = \frac{C_A V_A}{V_A + V_B}$	*5.78*
4	*30*	*Buffer solution (NH_4^+/NH_3)*	$pH = pK_a + log\left(\frac{[NH_3]}{[NH_4^+]}\right)$ $[NH_3] = \frac{C_B V_B - C_A V_A}{V_A + V_B}$, $[NH_4^+] = \frac{C_A V_A}{V_A + V_B}$	*8.95*