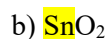


Exercise 1. Identify the oxidation number of the element labeled in yellow in each of the following compounds:



Solution:

To solve you just need to apply the simple rules:

- N_{OX} (H bound to non-metals) = +1

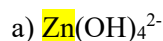
- N_{OX} (O bound to other atoms) = -2

- N_{OX} (atoms in molecules comprising just one element) = 0

- All molecules are non-charged so the total sum of all N_{OX} values adjusted by the corresponding coefficients should be 0 (net charge = 0).

a) +4; b) +4; c) -2; d) +5; e) +1; f) 0;

Exercise 2. Identify the oxidation number of the element labeled in yellow in each of the following ions:



Hint: Don't forget to take into consideration the ionic state.

Solution:

To solve you just need to apply the simple rules:

- N_{OX} (H bound to non-metals) = +1

- N_{OX} (O bound to other atoms) = -2

- N_{OX} (F bound to other atoms) = -1

- N_{OX} (Cl bound to other atoms in the absence of oxygen) = -1

- When calculating the N_{OX} you need to also consider the molecule charge. The sum of all N_{OX} values adjusted by the corresponding coefficients should be equal to the net charge.

a) +2; b) +2; c) +6; d) +4; e) +1;

Exercise 3. When atomic nickel (Ni) is added to CuCl_2 (aq), Ni^{2+} ions and atomic copper (Cu) form. When iron is added to NiCl_2 (aq), Fe^{2+} ions and atomic nickel (Ni) form.

- What will happen if atomic form of iron (Fe) is added to CuCl_2 (aq)? Explain.
- What are Fe and Cu^{2+} in the context of redox properties?
- If you wanted to restore Fe^{2+} back to Fe, could you achieve that using Cu or Ni as electron donors?

Solution:

a) Fe^{2+} ions and atomic copper (Cu) will form. Iron is able to reduce Ni^{2+} , meaning that it is a stronger reducing agent. Ni was able to reduce Cu^{2+} , which means that it is a stronger reducing agent. So, in terms of reducing properties: $\text{Fe} > \text{Ni} > \text{Cu}$.

b) Fe is the reducing agent (undergoes oxidation); Cu^{2+} is the oxidizing agent (undergoes reduction).

c) Not efficiently using just chemical potentials since Fe is a stronger reducing agent than Ni or Cu. But it may be possible using electrolytic approaches.

Exercise 4. Identify the oxidant and reductant in each of the following reactions:

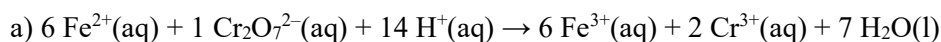
- $\text{Zn(s)} + 2 \text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(aq)}$ - A simple means of preparing H_2 gas in a lab.
- $2 \text{H}_2\text{S(g)} + \text{SO}_2\text{(g)} \rightarrow 3 \text{S(s)} + 2 \text{H}_2\text{O(l)}$ - A reaction used to produce sulfur.
- $\text{B}_2\text{O}_3\text{(s)} + 3 \text{Mg(s)} \rightarrow 2 \text{B(s)} + 3 \text{MgO(s)}$ - A reaction used to prepare elemental boron.
- $2 \text{N}_2\text{H}_4\text{(g)} + \text{N}_2\text{O}_4\text{(g)} \rightarrow 3 \text{N}_2\text{(g)} + 4 \text{H}_2\text{O(g)}$ - A reaction used to propel rockets

Solution:

- Oxidant: H^+ in HCl; Reductant: Zn;
- Oxidant: SO_2 ; Reductant: H_2S ;
- Oxidant: B_2O_3 ; Reductant: Mg;
- Oxidant: N_2O_4 ; Reductant: N_2H_4 ;

Exercise 5. Determine the stoichiometric coefficients of the following reactions:

- $\text{Fe}^{2+}\text{(aq)} + \text{Cr}_2\text{O}_7^{2-}\text{(aq)} + \text{H}^+\text{(aq)} \rightarrow \text{Fe}^{3+}\text{(aq)} + \text{Cr}^{3+}\text{(aq)} + \text{H}_2\text{O(l)}$
- $\text{Cr}_2\text{O}_3 + \text{NaNO}_3 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{CrO}_4 + \text{NaNO}_2 + \text{CO}_2$
- $\text{NaNO}_3 + \text{NaOH} + \text{Zn} \rightarrow \text{NH}_3 + \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$
- $\text{NaHSO}_4 + \text{Al} + \text{NaOH} \rightarrow \text{Na}_2\text{S} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$
- $\text{As}_4\text{O}_6 + \text{H}_2\text{O} + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_3\text{AsO}_4$

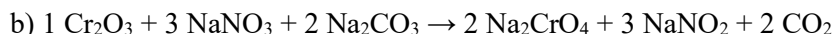
Solution:

Reductant: Fe^{2+} (N_{OX} of Fe changes from +2 to +3); Difference = -1 electrons

Oxidant: $\text{Cr}_2\text{O}_7^{2-}$ (N_{OX} of Cr changes from +6 to +3); Difference = +3 electrons * 2 (since $\text{Cr}_2\text{O}_7^{2-}$)

To balance: 1 $\text{Cr}_2\text{O}_7^{2-}$ is needed (= + 6 electrons) for 6 Fe^{2+} (= - 6 electrons)

The other components (e.g., H^+ and H_2O) are then balanced based on mass conservation.

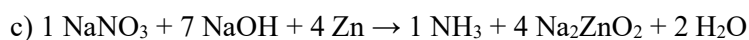


Reductant: Cr_2O_3 (N_{OX} of Cr changes from +3 to +6); Difference = -3 electrons * 2 (since Cr_2O_3)

Oxidant: NaNO_3 (N_{OX} of N changes from +5 to +3); Difference = +2 electrons

To balance: 1 Cr_2O_3 is needed (= - 6 electrons) for 3 NaNO_3 (= + 6 electrons)

Note that the N_{OX} of carbon does not change from left to right (= +4), but needs to be considered, and stoichiometric coefficients in Na_2CO_3 and CO_2 adjusted for mass conservation reasons.



Reductant: Zn (N_{OX} of Zn changes from 0 to +2); Difference = -2 electrons

Oxidant: NaNO_3 (N_{OX} of N changes from +5 to -3); Difference = +8 electrons

To balance: 4 Zn are needed (= - 8 electrons) for 1 NaNO_3 (= + 8 electrons)

The other components balanced based on mass conservation.

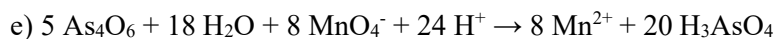


Reductant: Al (N_{OX} of Al changes from 0 to +3); Difference = -3 electrons

Oxidant: NaHSO_4 (N_{OX} of S changes from +6 to -2); Difference = +8 electrons

To balance: 8 Al are needed (= - 24 electrons) for 3 NaHSO_4 (= + 24 electrons)

The other components balanced based on mass conservation.



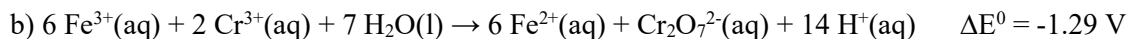
Reductant: As_4O_6 (N_{OX} of As changes from +3 to +5); Difference = -2 electrons * 4 (since As_4O_6)

Oxidant: MnO_4^- (N_{OX} of Mn changes from +7 to +2); Difference = +5 electrons

To balance: 8 MnO_4^- are needed (= + 40 electrons) for 5 As_4O_6 (= - 40 electrons)

The other components balanced based on mass conservation.

Exercise 6. Calculate the standard reaction Gibbs free energy for the following cell reactions:



$$F = 96485 \text{ C/mol}$$

Solution:

Here, you need to use the equation that connects the standard electromotive force (ΔE^0) and standard reaction Gibbs free energy (ΔG_r^0):

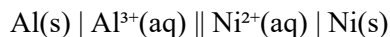
$$\Delta G_r^0 = -z \cdot F \cdot \Delta E^0$$

The value of z corresponds to the total number of electrons that got exchanged in a single redox reaction, and needs to be determined for each case.

a) $z = 2$; $\Delta G_r^0 = -2 \cdot 96485 \text{ C/mol} \cdot 1.08 \text{ V} = -208'407 \text{ C/mol} \cdot \text{J/C} = -208'407 \text{ J/mol}$

b) $z = 6$; $\Delta G_r^0 = -6 \cdot 96485 \text{ C/mol} \cdot (-1.29 \text{ V}) = 746'793 \text{ C/mol} \cdot \text{J/C} = 746'793 \text{ J/mol}$

Exercise 7. Consider the galvanic cell below:



- Write the corresponding half-reactions for each electrode.
- Assign which electrode will serve as cathode and which will serve as anode in this cell.
- What will be the direction of this reaction (i.e., which species will undergo oxidation and which species will be reduced)? Considering this, write a balanced chemical equation for this redox reaction.
- Calculate the standard electromotive force of the cell (ΔE^0).
- Calculate the ΔG_r^0 and determine if the reaction will favor reactants or products.
- Determine the equilibrium constant. What is that number suggesting about the reaction propensity under standard conditions.

The given values are:

$$E^0_{\text{Ni}^{2+}/\text{Ni}} = -0.257 \text{ V};$$

$$E^0_{\text{Al}^{3+}/\text{Al}} = -1.676 \text{ V}$$

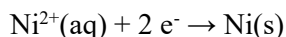
$$F = 96485 \text{ C/mol}$$

$$T = 298 \text{ K}$$

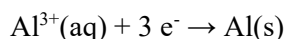
$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Solution:

a) Nickel (as a reduction):



Aluminum (as a reduction):



b) The species with the more positive standard reduction potential is reduced (cathode).

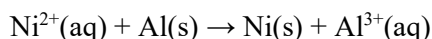
$$E^0_{\text{Ni}^{2+}/\text{Ni}} > E^0_{\text{Al}^{3+}/\text{Al}}$$

Therefore:

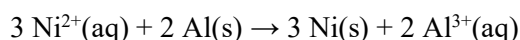
- **Cathode** (undergoing reduction): **Nickel** electrode

- **Anode** (undergoing oxidation): **Aluminium** electrode

c) To combine we first need to write the reaction taking into consideration the cathode/anode assignment performed in b):



Given that Ni exchange involves +2 electrons and Al exchange involves -3 electrons, the reaction can be balanced assuming that minimally 6 electrons are exchanged:



d) Standard electromotive force (ΔE^0) of the cell comprising these two electrodes is calculated by determining the difference between standard electrode potential (E^0) of the cathode and that of the anode:

$$\Delta E^0 = E^0(\text{cathode}) - E^0(\text{anode}) = E^0_{\text{Ni}^{2+}/\text{Ni}} - E^0_{\text{Al}^{3+}/\text{Al}} = \mathbf{1.419\text{ V}}$$

e) Using the formula for ΔG_r^0 :

$$\Delta G_r^0 = -z \cdot F \cdot \Delta E^0 = -6 \cdot 96485\text{ C/mol} \cdot 1.419\text{ J/C} = \mathbf{-821'473\text{ J/mol}}$$

Because ΔG_r^0 is large and negative, the reaction is strongly spontaneous under standard conditions and therefore favors products (formation of Ni(s) and Al^{3+} ions) at standard state.

f) Given that:

$$\Delta G_r^0 = R \cdot T \cdot \ln(K) \quad \rightarrow \quad K = e^{\{-\Delta G_r^0/(R \cdot T)\}} = 9.9 \cdot 10^{143}$$

An astronomically large number. This number shows that under standard solution conditions, the equilibrium will **STRONGLY** favor the products.

Exercise 8. Consider the Daniell cell made of a zinc plate immersed in a solution of ZnSO_4 whose activity of Zn^{2+} is 1 (concentration = 1 mol/L), and a copper plate immersed in a solution of CuSO_4 ; the two electrodes are connected by a salt bridge. When the current is zero (high-resistance voltmeter used), the potential difference measured between the terminals of the cell is $\Delta E = 1.02\text{ V}$.

- Is the system operating under standard conditions? Explain your rationale.
- What is the potential of the Zn^{2+}/Zn and Cu^{2+}/Cu electrodes?
- Calculate the concentration of Cu^{2+} in the second compartment (assuming that it perfectly matches Cu^{2+} activity).

The given values:

$$E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.762\text{ V};$$

$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.342\text{ V}$$

$$T = 298\text{ K, atmospheric pressure.}$$

$$F = 96485\text{ C/mol}$$

$$R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$$

Solution:

a) We already can see that the concentration has only been specified for ZnSO_4 (activity = 1) but not for CuSO_4 . This may mean that the CuSO_4 concentration is non-standard. But to check we have to look at the measured cell potential (ΔE) and compare it to the standard electromotive force (ΔE^0) of the cell:

$$\Delta E^0 = E^0(\text{cathode}) - E^0(\text{anode})$$

Given that: $E^\circ(\text{Cu}^{2+}/\text{Cu}) > E^\circ(\text{Zn}^{2+}/\text{Zn})$, the Cu electrode will serve as a cathode. Hence:

$$\Delta E^0 = 0.342\text{ V} - (-0.762\text{ V}) = \mathbf{1.104\text{V}}$$

If we consider that the measured potential ΔE is different from ΔE^0 , we can conclude that the galvanic cell is operating under non-standard conditions.

b) Based on the question text, the concentration of ZnSO_4 is 1 mol/L (activity = 1) which, given the standard temperature and pressure, means that the Zn^{2+}/Zn electrode is operating under standard conditions. That means that:

$$E(\text{Zn}^{2+}/\text{Zn}) = E^0(\text{Zn}^{2+}/\text{Zn}) = \mathbf{-0.762}$$

On the other hand, the concentration of CuSO_4 is not specified in the question text. So we can infer that the lower overall cell potential is due to the fact that Cu is operating under non-standard conditions.

The electrode potential for Cu electrode can be calculated by considering the cell potential (ΔE) and $E(\text{Zn}^{2+}/\text{Zn})$:

$$E(\text{Cu}^{2+}/\text{Cu}) = \Delta E - E(\text{Zn}^{2+}/\text{Zn}) = 1.02 \text{ V} + (-0.762 \text{ V}) = \mathbf{0.258 \text{ V}}$$

c) Here we can use the Nernst equation:

$$\Delta E = \Delta E^0 - R \cdot T \cdot \ln Q / (z \cdot F)$$

Which describes the entire galvanic cell comprising Cu and Zn electrodes. If we solve for Q we get:

$$\ln Q = (\Delta E^0 - \Delta E) \cdot z \cdot F / (R \cdot T) = 6.54 \quad \rightarrow \quad \mathbf{Q = 694.0}$$

If we consider the reaction direction, for this electrode pair we get that:

$$Q = [\text{Zn}^{2+}] / [\text{Cu}^{2+}] \quad \rightarrow \quad [\text{Cu}^{2+}] = [\text{Zn}^{2+}] / Q = 1 / 694.0 = \mathbf{1.44 \cdot 10^{-3} \text{ mol/L}}$$

Alternatively, you could have also used the standard electrode potential for Cu electrode and use this form of the equation:

$$E(\text{Cu}^{2+}/\text{Cu}) = E^0(\text{Cu}^{2+}/\text{Cu}) + R \cdot T \cdot \ln Q / (z \cdot F)$$

Which assumes Cu^{2+}/Cu is coupled to the SHE. This would also lead to the correct solution, but you have to be careful about defining the direction of redox reaction since that will influence how Q is calculated.

Exercise 9. Consider the thermodynamic cell at 25 °C composed of two electrodes connected by a salt bridge: the first is a copper strip immersed in 1 liter of a $\text{Cu}(\text{NO}_3)_2$ solution in which the activity of Cu^{2+} is 1 (concentration = 1 mol/L), and the second electrode is also a copper strip immersed in 1 liter of a $\text{Cu}(\text{NO}_3)_2$ solution in which the activity of Cu^{2+} is 5×10^{-4} (concentration = 5×10^{-4} mol/L).

- In this cell system, what is the cathode and what is the anode?
- Determine the potential difference (ΔE) between the two electrodes when the current is zero (i.e., high resistance voltmeter used).
- What are the concentrations of Cu^{2+} in the two compartments (electrodes) when the cell is fully discharged (dead)?
- What is then the change in mass of the two copper strips when the cell is fully discharged?

Solution.

The given values:

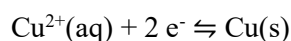
$$E^0(\text{Cu}^{2+}/\text{Cu}) = 0.342 \text{ V}$$

$$F = 96485 \text{ C/mol}$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$M(\text{Cu}) = 63.546 \text{ g mol}^{-1}$$

a) This is a so-called concentration cell where both electrodes have the same components but at different concentrations. Given that:



$$[\text{Cu}^{2+}]_1 = 1 \text{ mol/L} > [\text{Cu}^{2+}]_2 = 5 \cdot 10^{-4} \text{ mol/L}$$

To reach equilibrium, the system will tend to move both sides towards equal concentration (reducing $[Cu^{2+}]_1$ and increasing $[Cu^{2+}]_2$). Therefore, we have:

- Compartment 1 ($[Cu^{2+}]_1 = 1 \text{ mol/L}$) will favor reduction and serve as a **cathode**.
- Compartment 2 ($[Cu^{2+}]_2 = 5 \cdot 10^{-4} \text{ mol/L}$) will favor oxidation and serve as an **anode**.

b) Considering the electrode assignment in the first paragraph we will have:

$$\Delta E = E (\text{cathode}) - E (\text{anode})$$

If we use the Nernst equation for each electrode:

$$E = E^0 (\text{Cu}^{2+}/\text{Cu}) - R \cdot T \cdot \ln Q / (z \cdot F)$$

And assume that for this chemical equation: $\text{Cu}^{2+}(\text{aq}) + 2 e^- \rightleftharpoons \text{Cu}(\text{s})$:

$$Q = 1 / [Cu^{2+}]$$

We get that:

$$E (\text{cathode}) = 0.342 \text{ V}$$

$$E (\text{anode}) = 0.244 \text{ V}$$

By using these values we get:

$$\Delta E = E (\text{cathode}) - E (\text{anode}) = 0.098 \text{ V} = 98 \text{ mV}$$

c) When the cell is dead, there is no net flow of electrons through the circuit. That means that the system has reached a state where both electrodes produce the same potential:

$$\Delta E = E (\text{cathode}) - E (\text{anode}) = 0$$

$$E (\text{cathode}) = E (\text{anode})$$

If we apply the Nernst equation for both sides, and we apply the equation for Q, we get:

$$E^0 (\text{Cu}^{2+}/\text{Cu}) + R \cdot T \cdot \ln [Cu^{2+}]_1 / (z \cdot F) = E^0 (\text{Cu}^{2+}/\text{Cu}) + R \cdot T \cdot \ln [Cu^{2+}]_2 / (z \cdot F)$$

Cancelling the equal parts on both sides gives us:

$$\ln [Cu^{2+}]_1 = \ln [Cu^{2+}]_2 \quad \rightarrow \quad [Cu^{2+}]_1 = [Cu^{2+}]_2$$

Given that the total amount of Cu^{2+} across both solutions is conserved:

$$[Cu^{2+}]_1 \cdot V_1 + [Cu^{2+}]_2 \cdot V_2 = 1 \text{ mol} + 5 \cdot 10^{-4} \text{ mol} = 1.0005 \text{ mol}$$

When the system is discharged each of the two electrodes gets $\frac{1}{2}$ of this total amount:

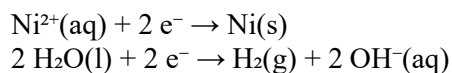
$$[Cu^{2+}]_1 = [Cu^{2+}]_2 = 0.50025 \text{ mol/L}$$

d) Due to the reduction of Cu^{2+} from solution, the cathode will gain more solid Cu. Conversely, due to the oxidation of Cu in the electrode, the anode will lose some Cu, creating $\text{Cu}^{2+}(\text{aq})$. Given the quantities we just estimated in c), we get that:

$$\text{- Cathode gained } 0.49975 \text{ mol of Cu} \rightarrow m = 0.49975 \text{ mol} \cdot 63.546 \text{ g mol}^{-1} = 31.76 \text{ g}$$

$$\text{- Anode lost } 0.49975 \text{ mol of Cu} \rightarrow m = 0.49975 \text{ mol} \cdot 63.546 \text{ g mol}^{-1} = 31.76 \text{ g}$$

Exercise 10. Ni electrodes can often cause the reduction of H₂O and formation of H₂ gas during normal operation. Let's assume that you have such electrode connected into an electrolytic cell. A current of 15 A is used to deposit solid Ni from an aqueous solution of NiSO₄. Nickel metal and hydrogen gas form simultaneously at the same electrode according to the reactions below. The system uses 60% of the current to produce Ni and 40% to produce H₂.



- a) What is the mass of Ni deposited during 1 hour?
b) What is the volume of H₂ released at 25 °C and the pressure of 1 bar during the same time? Assume that H₂ is a perfect gas .

Given values:

$$\begin{aligned}F &= 96485 \text{ C/mol} \\ R &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \\ M(\text{Ni}) &= 58.693 \text{ g mol}^{-1} \\ M(\text{H}) &= 1.0078 \text{ g mol}^{-1}\end{aligned}$$

Solution.

a) Here we simply apply the Faraday equation:

$$n = I \cdot t / (z \cdot F) \quad \rightarrow \quad m(\text{Ni}) = M(\text{Ni}) \cdot I \cdot t / (z \cdot F)$$

For the Ni reaction above: $z = 2$; $t = 3600 \text{ s}$; and the other values are given. So, the theoretical maximum amount of Ni produced under these conditions is:

$$m(\text{Ni})^* = 16.42 \text{ g} \quad \rightarrow \quad * \text{ theoretical max}$$

However, this number needs to be adjusted by a factor of 0.6 because only 60% of current was applied towards the production of Ni. With the adjustment the final quantity is:

$$m(\text{Ni}) = 16.42 \text{ g} \cdot 0.6 = \mathbf{9.85\text{g}}$$

b) Here the goal is to calculate the volume of H₂ released. First, we apply the Faraday equation to estimate the theoretical number of moles of H₂ if the reaction was 100% efficient in producing H₂.

$$n = I \cdot t / (z \cdot F) \quad \rightarrow \quad n(\text{H}_2)^* = 15 \cdot 3600 / (2 \cdot 96485) \text{ mol} = 0.28 \text{ mol}$$

When adjusted by a factor of 0.4, due to the 40% current usage, the total amount of H₂ generated is:

$$n(\text{H}_2) = 0.28 \text{ mol} \cdot 0.4 = 0.112 \text{ mol}$$

From the perfect gas equation:

$$p \cdot V(\text{H}_2) = n(\text{H}_2) \cdot R \cdot T \quad \rightarrow \quad V(\text{H}_2) = 0.112 \text{ mol} \cdot 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K} / 100'000 \text{ Pa}$$

$$V(\text{H}_2) = 0.00277 \text{ J Pa}^{-1} = 0.00277 \text{ m}^3 = \mathbf{2.77 \text{ L}}$$
