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

a) H_4SiO_4

b) SnO_2

c) N_2H_4

d) P_4O_{10}

e) S_2Cl_2

f) P_4

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

a) $Zn(OH)_4^{2-}$

b) $PdCl_4^{2-}$

c) UO_2^{2+}

d) SiF_6^{2-}

e) IO^-

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

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.

a) What will happen if atomic form of iron (Fe) is added to $CuCl_2$ (aq)? Explain.

b) What are Fe and Cu^{2+} in the context of redox properties?

c) If you wanted to restore Fe^{2+} back to Fe, could you achieve that using Cu or Ni as electron donors?

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

a) $Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(aq)$ - A simple means of preparing H_2 gas in a lab.

b) $2\ H_2S(g) + SO_2(g) \rightarrow 3\ S(s) + 2\ H_2O(l)$ - A reaction used to produce sulfur.

c) $B_2O_3(s) + 3\ Mg(s) \rightarrow 2\ B(s) + 3\ MgO(s)$ - A reaction used to prepare elemental boron.

d) $2\ N_2H_4(g) + N_2O_4(g) \rightarrow 3\ N_2(g) + 4\ H_2O(g)$ - A reaction used to propel rockets

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

a) $Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + H^+(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq) + H_2O(l)$

b) $Cr_2O_3 + NaNO_3 + Na_2CO_3 \rightarrow Na_2CrO_4 + NaNO_2 + CO_2$

c) $NaNO_3 + NaOH + Zn \rightarrow NH_3 + Na_2ZnO_2 + H_2O$

d) $NaHSO_4 + Al + NaOH \rightarrow Na_2S + Al_2O_3 + H_2O$

e) $As_4O_6 + H_2O + MnO_4^- + H^+ \rightarrow Mn^{2+} + H_3AsO_4$

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

a) $2\ Ce^{4+}(aq) + 3\ I^-(aq) \rightarrow 2\ Ce^{3+}(aq) + I_3^-(aq)$ $\Delta E^0 = +1.08$ V

b) $6\ Fe^{3+}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l) \rightarrow 6\ Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq)$ $\Delta E^0 = -1.29$ V

F = 96485 C/mol

Exercise 7. Consider the galvanic cell below:

$Al(s) \mid Al^{3+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$

a) Write the corresponding half-reactions for each electrode.

b) Assign which electrode will serve as cathode and which will serve as anode in this cell.

c) 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.

d) Calculate the standard electromotive force of the cell (ΔE^0).

e) Calculate the ΔG_r^0 and determine if the reaction will favor reactants or products.

f) Determine the equilibrium constant. What is that number suggesting about the reaction propensity under standard conditions.

The given values are:

$E^0_{Ni2+/Ni} = -\ 0.257$ V;
$E^0_{Al3+/Al} = -\ 1.676$ V
F = 96485 C/mol
T = 298 K
R = 8.314 J mol^{-1} K^{-1}

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 $\Delta E = 1.02$ V.

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

The given values:

$E°(Zn^{2+}/Zn) = -0.762$ V ;
$E°(Cu^{2+}/Cu) = 0.342$ V
T = 298 K, atmospheric pressure.
F = 96485 C/mol
$R = 8.314$ J mol^{-1} K^{-1}

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 $Cu(NO_3)_2$ 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 $Cu(NO_3)_2$ solution in which the activity of Cu^{2+} is 5×10^{-4} (concentration = 5×10^{-4} mol/L).

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

Exercise 10. Ni electrodes can often cause the reduction of H_2O and formation of H_2 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 $NiSO_4$. 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 H_2.

$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

a) What is the mass of Ni deposited during 1 hour?
b) What is the volume of H_2 released at 25 °C and the pressure of 1 bar during the same time? Assume that H_2 is a perfect gas .

Given values:

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

Quick Answers:

1.

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

2.

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

3.

a) Fe^{2+} and Cu will form. b) Fe is the reducing agent; Cu^{2+} is the oxidizing agent. c) No.

4.

a) Oxidant: H^+ in HCl; Reductant: Zn;
b) Oxidant: SO_2; Reductant: H_2S;
c) Oxidant: B_2O_3; Reductant: Mg;
d) Oxidant: N_2O_4; Reductant: N_2H_4;

5.

a) 6 $Fe^{2+}(aq)$ + 1 $Cr_2O_7^{2-}(aq)$ + 14 $H^+(aq)$ → 6 $Fe^{3+}(aq)$ + 2 $Cr^{3+}(aq)$ + 7 $H_2O(l)$
b) 1 Cr_2O_3 + 3 $NaNO_3$ + 2 Na_2CO_3 → 2 Na_2CrO_4 + 3 $NaNO_2$ + 2 CO_2
c) 1 $NaNO_3$ + 7 NaOH + 4 Zn → 1 NH_3 + 4 Na_2ZnO_2 + 2 H_2O
d) 3 $NaHSO_4$ + 8 Al + 3 NaOH → 3 Na_2S + 4 Al_2O_3 + 3 H_2O
e) 5 As_4O_6 + 18 H_2O + 8 MnO_4^- + 24 H^+ → 8 Mn^{2+} + 20 H_3AsO_4

6.

a) ΔG_r^0 = - 208'407 J/mol

b) ΔG_r^0 = 746'793 J/mol

7.

a) $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$

$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$

b) Cathode: Nickel

Anode: Aluminium

c) 3 $Ni^{2+}(aq)$ + 2 Al(s) → 3 Ni(s) + 2 $Al^{3+}(aq)$

d) ΔE^0 = 1.419 V

e) ΔG_r^0 = - 821'473 J/mol; Strongly favouring products

f) K = 9.9 • 10^{143}; The reaction will STRONGLY favor the products.

8.

a) No, since ΔE^0 is not equal to ΔE.
b) E (Zn^{2+}/Zn) = -0.762; E (Cu^{2+}/Cu) = 0.258 V;
c) $[Cu^{2+}]$ = 1.44 • 10^{-3} mol/L

9.

a) Compartment 1 ($[Cu^{2+}]_1$ = 1 mol/L) – cathode; Compartment 2 ($[Cu^{2+}]_2 = 5\cdot10^{-4}$ mol/L) – anode.
b) ΔE^0 = 0.098 V
c) $[Cu^{2+}]_1 = [Cu^{2+}]_2$ = 0.50025 mol/L
d) Cathode gained 31.76 g; Anode lost 31.76 g;

10.

a) m (Ni) = 9.85 g
b) $V(H_2)$ = 2.77 L