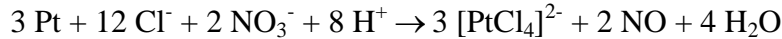


1. a. $E^\circ_{\text{cell}}=0.201 \text{ V}$ for the reaction



What is E° for the reduction of $[\text{PtCl}_4]^{2-}$ to Pt in acidic solution?

The standard reduction potential for the Nitrate ion to Nitrogen Monoxide is $+0.96 \text{ V}$.

Because the Nitrate is reduced in the equation it is the cathode. $\text{Pt}/[\text{PtCl}_4]^{2-}$ is the anode.

$$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}} \quad E_{\text{an}} = E_{\text{cat}} - E_{\text{cell}} = +0.96 \text{ V} - 0.201 \text{ V} = 0.76 \text{ V}$$

b. Calculate the pH required to have $E_{\text{cell}} = 0.072 \text{ V}$ when $[\text{NO}_3^-] = 1.15 \text{ M}$, $[\text{Cl}^-] = 3.22 \text{ M}$, $[\text{PtCl}_4^{2-}] = 0.03 \text{ M}$, and $P_{\text{NO}} = 0.22 \text{ atm}$.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \frac{P_{\text{NO}}^2 ([\text{PtCl}_4]^{2-})^3}{[\text{Cl}^-]^{12} [\text{NO}_3^-]^2 [\text{H}^+]^8}$$

$$-\frac{nF(E_{\text{cell}} - E^\circ_{\text{cell}})}{RT} = \ln \frac{P_{\text{NO}}^2 ([\text{PtCl}_4]^{2-})^3}{[\text{Cl}^-]^{12} [\text{NO}_3^-]^2 [\text{H}^+]^8} = 30.1270 = \ln \frac{(0.22)^2 (0.03)^3}{(3.22)^{12} (1.15)^2 [\text{H}^+]^8} = \ln 7.9532 \times 10^{-13} - 8 \ln [\text{H}^+]$$

$$\frac{30.1270 - \ln 7.9532 \times 10^{-13}}{8} = \frac{30.1270 - (-27.8600)}{8} = \frac{57.9870}{8} = 7.24837 = -\ln [\text{H}^+]$$

$$[\text{H}^+] = e^{-7.24837} = 7.11 \times 10^{-4} \Rightarrow pH = 3.14 = 3.1$$

2. A process has a standard change in enthalpy of +45.66 kJ. What must be the *minimum standard change in entropy* for this process to be spontaneous?

The ΔG for the process must be less than zero for it to be spontaneous:

$$\Delta G = \Delta H - T\Delta S < 0$$

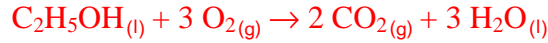
$$\Delta S > \frac{\Delta H}{T} = \frac{45.66 \times 10^3 \text{ J}}{298.15 \text{ K}} = 153.1 \text{ J K}^{-1}$$

3. Calculate *the mass of Zn* deposited at the cathode in 42.5 min when 1.87 A of current is passed through an aqueous solution of Zn^{2+} .

$$42.5 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1.87 \text{ C}}{\text{s}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Zn}}{2 \text{ mol e}^-} \times \frac{65.38 \text{ g Zn}}{1 \text{ mol Zn}} = 1.62 \text{ g Zn}$$

4. 0.5334 g of ethanol, C_2H_5OH , is burned in a bomb calorimeter with a heat capacity of $12.44 \text{ kJ } ^\circ\text{C}^{-1}$. The temperature increased from 17.66°C to 18.93°C .

a. Calculate the *standard molar enthalpy change* for the combustion of ethanol.



$$q_{v,cal} = C\Delta T = (12.44 \text{ kJ } ^\circ\text{C}^{-1})(18.93^\circ\text{C} - 17.66^\circ\text{C}) = 15.79 \text{ kJ} = -q_{v,rxn}$$

$$\Delta U = \frac{q_{v,rxn}}{n_{C_2H_5OH}} = \frac{-15.79 \text{ kJ}}{(0.5334 \text{ g})\left(\frac{1 \text{ mol } C_2H_5OH}{46.0684 \text{ g } C_2H_5OH}\right)} = -1363.74 \text{ kJ mol}^{-1}$$

$$\Delta H = \Delta U + \Delta nRT = -1363.74 \text{ kJ mol}^{-1} + \left(\frac{-1 \text{ mol gas}}{\text{mol}}\right)\left(\frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mol gas K}}\right)(298.15 \text{ K})$$

$$= -1366.23 \text{ kJ mol}^{-1} = -1.37 \times 10^3 \text{ kJ mol}^{-1}$$

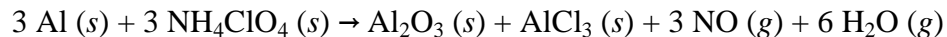
b. The heat of formation of Carbon Dioxide is $-393.5 \text{ kJ mol}^{-1}$ and that of liquid water is $-285.840 \text{ kJ mol}^{-1}$. What is the *heat of formation of ethanol in kJ mol^{-1}* ?

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

$$-1.37 \times 10^3 \text{ kJ mol}^{-1} = [(2)(-393.5 \text{ kJ mol}^{-1}) + (3)(-285.840 \text{ kJ mol}^{-1})] - [(1)\Delta H_f^\circ(C_2H_5OH) + (3)(0.0 \text{ kJ mol}^{-1})]$$

$$\Delta H_f^\circ = -1.37 \times 10^3 \text{ kJ mol}^{-1} - [(2)(-393.5 \text{ kJ mol}^{-1}) + (3)(-285.840 \text{ kJ mol}^{-1})] = 274.52 \text{ kJ mol}^{-1} = 2.7 \times 10^2 \text{ kJ mol}^{-1}$$

5. The solid fuel boosters for the space shuttle utilize the following reaction:



Given:

Substance	ΔG_f° (kJ mol ⁻¹)
NH ₄ ClO ₄ (s)	-89
Al ₂ O ₃ (s)	-1582
AlCl ₃ (s)	-629
NO (g)	52
H ₂ O (g)	-229

Calculate the *thermodynamic equilibrium constant at 25 °C* for the reaction.

$$\Delta G_{rxn} = [(1)(-1582) + (1)(-629) + (3)(52) + (6)(-229)] - [(3)(0) + (3)(-89)]$$
$$= -3162 \text{ kJ mol}^{-1}$$

$$K = e^{-\frac{\Delta G}{RT}} = e^{-\frac{-3162 \times 10^3}{(8.314)(298.15)}} = e^{1275.60} = 10^x \Rightarrow x = \frac{1275.60}{\ln 10} = 553.9 = 554$$

$$K = 10^{554}$$

6. **Identify** the following substances based on the given results of the chemical tests.

a. A white precipitate forms under slightly basic conditions when Strontium Nitrate is added. A small amount of white precipitate forms slowly with the addition of Silver Nitrate. Addition of Potassium Permanganate and extraction with cyclohexane gives a dark purple aqueous layer and a colorless organic layer. Flame tests give a greenish flame. Under acidic conditions, addition of Thioacetamide gives a black precipitate that dissolves with Nitric acid. The buffered solution gives a maroon precipitate when Potassium Hexacyanoferrate(II) is added.

Unknown “a” is **CuSO₄ Copper(II) Sulfate** (give the **name** and **formula**)

b. A white precipitate forms with the addition of calcium and silver. Addition of Potassium Permanganate and extraction with cyclohexane gives colorless aqueous and organic layers. Addition of thioacetamide gives a black precipitate. Addition of Ammonium Hydroxide gives a greenish precipitate. This precipitate dissolves in Hydrogen Peroxide to give a yellow solution that has a yellow precipitate with the addition of Lead(II) Nitrate.

Unknown “b” is **Cr₂(C₂O₄)₃ Chromium(III) Oxalate** (give the **name** and **formula**)

c. A solution is known to contain Iron(III) ions and Calcium ions.

i. Give **ONE and only ONE** test that will separate these two ions. Which ion is in the supernatant and which is in the precipitate?

Add ammonium hydroxide: The Iron will precipitate as Fe(OH)₃, the calcium will stay in solution.

ii. Give **ONE and only ONE** test that will confirm the presence of the Iron(III) ion. Will this test be performed on the supernatant or the precipitate?

Acidify and add KSCN to the precipitate. The red-maroon color indicates the presence of Fe³⁺

iii. Give **ONE and only ONE** test that will confirm the presence of the Calcium ion. Will this test be performed on the supernatant or the precipitate?

Add Ammonium Carbonate to the supernatant. A white precipitate will confirm the presence of Ca²⁺

6. (continued) d. Multiple Choice. Write the letter corresponding to the ***BEST*** choice(s) in the blank provided. Not following direction WILL result in losing points.

 c i. Which of the following ions will form a red solution with KSCN?
a. Fe^{2+} b. Cu^{2+} c. Fe^{3+} d. Li^+

 a and d ii. Which of the following ions requires basic Hydrogen Peroxide for the separation test?
a. Fe^{3+} b. Cu^{2+} c. K^+ d. Cr^{3+}

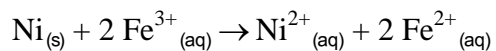
 b iii. Which of the following ions will give a white precipitate with the addition of thioacetamide?
a. Fe^{3+} b. Zn^{2+} c. Cu^{2+} d. Ag^+

 a iv. Which of the following ions gives a yellow color in the flame test?
a. Na^+ b. Ca^{2+} c. K^+ d. Li^+

 c v. Which of the following ions will form a red precipitate with $\text{K}_4\text{Fe}(\text{CN})_6$?
a. Li^+ b. Zn^{2+} c. Cu^{2+} d. Cr^{3+}

7. Use electrode potentials to answer the following questions. Justify your answers with calculations.

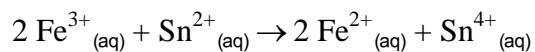
a. Is the oxidation of nickel by iron(III) ion a spontaneous reaction under standard reaction conditions?



$$E_{cell}^{\circ} = E_{cat}^{\circ} - E_{an}^{\circ} = +0.77 \text{ V} - (-0.25 \text{ V}) = +1.02 \text{ V}$$

The positive cell potential indicates that the reaction is spontaneous as written.

b. Will iron(III) ion oxidize tin(II) ion to tin(IV) ion under standard conditions?



$$E_{cell}^{\circ} = E_{cat}^{\circ} - E_{an}^{\circ} = +0.77 \text{ V} - (+0.15 \text{ V}) = +0.62 \text{ V}$$

The positive cell potential indicates that the reaction is spontaneous as written.