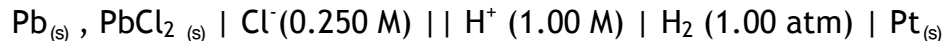


1. Determine the emf of the following cell

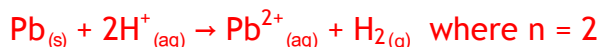


The anode is essentially a lead electrode,  $\text{Pb}^{2+}_{(aq)} \mid \text{Pb}_{(s)}$ . However, the anode solution is saturated with Lead(II) Chloride, so that the Lead(II) ion concentration is determined by the solubility product of Lead(II) Chloride ( $K_{sp} = 1.6 \times 10^{-5}$ )

First determine the concentration of  $\text{Pb}^{2+}$  ions.

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 \therefore [\text{Pb}^{2+}] = \frac{K_{sp}}{[\text{Cl}^-]^2} = \frac{1.6 \times 10^{-5}}{(0.250)^2} = 2.56 \times 10^{-4} \text{ M}$$

The overall chemical equation is essentially:

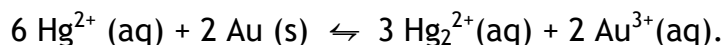


$E^\circ_{\text{cell}}$  can be determined from the data in the standard reduction potential table.  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.00 \text{ V} - (-0.17 \text{ V}) = +0.17 \text{ V}$

Then we have:

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Pb}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2} \\ &= 0.17 \text{ V} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(2 \text{ mol e}^-/\text{mol})(96485 \text{ C (mol e}^-)^{-1})} \ln \frac{[2.54 \times 10^{-4}](1.00)}{[1.00]^2} = 0.28 \text{ V} \end{aligned}$$

2. Using half-cell potentials, calculate the equilibrium constant at 25°C for



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.920 \text{ V} - 1.42 \text{ V} = -0.50 \text{ V}$$

$$K = e^{nFE^{\circ}/RT} = e^{(6)(96485)(-0.50)/(8.314)(298.15)} = 1.935 \times 10^{-51}$$

If 1.00 L of a 1.00 M  $\text{Au}(\text{NO}_3)_3$  solution is added to 1.00 L of a 1.00 M  $\text{Hg}_2(\text{NO}_3)_2$  solution, calculate the concentrations of Mercury(II), Mercury(I), and Gold(III) at equilibrium.

$K$  is infinite so let's let the reaction go to completion in the *reverse* direction then come back to equilibrium.

	$\text{Hg}_2^{2+}$	$\text{Hg}_2^{2+}$	$\text{Au}^{3+}$
I	0.00	0.50	0.50
Comp	1.00	-0.50	-0.33
C	-x	+x	+x
E	1.00-x	x	0.17+x

$$K = 1.9 \times 10^{-51} = \frac{[\text{Hg}_2^{2+}]^3 [\text{Au}^{3+}]^2}{[\text{Hg}_2^{2+}]^6} = \frac{[x]^3 [0.17+x]^2}{[1.00-x]^6} \approx \frac{x^3 (0.17)^2}{(1.00)^6}$$

We make this assumption because  $K$  is so small. The assumption is valid.

$$x = \sqrt[3]{\frac{1.9 \times 10^{-51}}{(0.17)^2}} = 4.0 \times 10^{-17} \text{ M}$$

$$[\text{Hg}_2^{2+}] = 1.00 - x = 1.00 \text{ M}; [\text{Hg}_2^{2+}] = x = 4.0 \times 10^{-17} \text{ M}; [\text{Au}^{3+}] = 0.17 + x = 0.17 \text{ M}$$

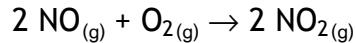
3. Calculate the entropy change when 1.00 mol of water boils at its boiling point.  $\Delta H_{\text{vap}} = 40.7 \text{ kJ mol}^{-1}$  for water.

$$\Delta S = \frac{\Delta H}{T} = \frac{40.7 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K}} = 109 \text{ J mol}^{-1} \text{ K}^{-1}$$

What is the free energy change for this process? Explain or show calculations.

$\Delta G$  is 0 because a phase transition at the phase transition temperature is an equilibrium process.

4. You have the following reaction at 250°C.



a. Determine if the reaction is spontaneous at this temperature.

$$\begin{aligned} \Delta H &= \sum_{\text{products}} n\Delta H_f^\circ - \sum_{\text{reactants}} n\Delta H_f^\circ \\ &= \left[ \left( \frac{2 \text{ mol NO}_2}{\text{mol rxn}} \right) \left( \frac{33.18 \text{ kJ}}{\text{mol NO}_2} \right) \right] - \left[ \left( \frac{2 \text{ mol NO}}{\text{mol rxn}} \right) \left( \frac{90.25 \text{ kJ}}{\text{mol NO}} \right) + \left( \frac{1 \text{ mol O}_2}{\text{mol rxn}} \right) \left( \frac{0.00 \text{ kJ}}{\text{mol O}_2} \right) \right] = -114.14 \text{ kJ mol}^{-1} \\ \Delta S &= \sum_{\text{products}} nS^\circ - \sum_{\text{reactants}} nS^\circ \\ &= \left[ \left( \frac{2 \text{ mol NO}_2}{\text{mol rxn}} \right) \left( \frac{240.06 \text{ J}}{\text{mol NO}_2 \text{ K}} \right) \right] - \left[ \left( \frac{2 \text{ mol NO}}{\text{mol rxn}} \right) \left( \frac{210.761 \text{ J}}{\text{mol NO K}} \right) + \left( \frac{1 \text{ mol O}_2}{\text{mol rxn}} \right) \left( \frac{205.138 \text{ J}}{\text{mol O}_2 \text{ K}} \right) \right] = -146.54 \text{ J mol}^{-1} \text{ K}^{-1} \\ \Delta G &= \Delta H - T\Delta S = (-114.14 \text{ kJ mol}^{-1}) - (523 \text{ K}) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) (-146.54 \text{ J mol}^{-1} \text{ K}^{-1}) = -37.50 \text{ kJ} \end{aligned}$$

The reaction is spontaneous at this temperature.

b. If the reaction is not spontaneous at this temperature, calculate the temperature at which it becomes spontaneous.

NA

c. Calculate the equilibrium constant for this reaction at 250°C.

$$K = e^{-\frac{\Delta G}{RT}} = e^{-\frac{(-37.50 \text{ kJ mol}^{-1})}{(8.314 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-1})(523 \text{ K})}} = 5.53 \times 10^3$$

5. You have decided to take a job as an electroplater. (I don't really know why, just go along with it.) A person with a hot rod comes in and wants you to plate his bumper, which has an area of  $1.50 \times 10^3 \text{ cm}^2$ , with Chromium (density =  $7.14 \text{ g/cm}^3$ ). The thickness of the plating is to be  $0.010 \text{ cm}$ . Your apparatus can generate only  $10.00 \text{ amps}$  and you have a solution of Chromium(VI) chloride. In how many hours should the person return to pickup his bumper?

$$\begin{aligned}
 ? \text{ h} &= (1.50 \times 10^3 \text{ cm}^2)(0.010 \text{ cm}) \times \frac{7.14 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \times \frac{6 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96485 \text{ C}}{1 \text{ mol e}^-} \\
 &\quad \times \frac{1 \text{ s}}{10.00 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 33.1 \text{ h}
 \end{aligned}$$

6. A reaction takes place in a cylinder fitted with a piston. The entire cylinder is placed into a  $500.0 \text{ g}$  water bath at  $15.3^\circ\text{C}$ . The external pressure is  $768.3 \text{ mmHg}$ . Before the reaction takes place, the volume in the cylinder is  $256.3 \text{ mL}$ . After the reaction the volume of the cylinder is  $879.2 \text{ mL}$  and the temperature of the water bath is  $28.6^\circ\text{C}$ . Calculate:

a.  $q$

$$\begin{aligned}
 q &= -ms\Delta T = -(500.0 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(28.6^\circ\text{C} - 15.3^\circ\text{C}) = -27823.6 \text{ J} \\
 &= -2.78 \times 10^4 \text{ J}
 \end{aligned}$$

b.  $w$

$$\begin{aligned}
 w &= -P_{\text{ext}}\Delta V = -(768.3 \text{ mmHg})(879.2 \text{ mL} - 256.3 \text{ mL}) \left( \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{101.325 \text{ J}}{1 \text{ L atm}} \right) \\
 &= 63.804628 \text{ J}
 \end{aligned}$$

c.  $\Delta H = q = -2.78 \times 10^4 \text{ J}$

d.  $\Delta U = q + w = -2.78 \times 10^4 \text{ J} + 63.80 \text{ J} = -2.78 \times 10^4 \text{ J}$

7. Qualitative analysis:

A. Multiple Choice: Write the letter of the **best answer** in the space provided. **Circling your answer will NOT count.**

a i. Which of the following is used to separate Silver ions from Copper(II) ions?

- a.  $\text{Cl}^-$       b.  $\text{K}_4\text{Fe}(\text{CN})_6$       c.  $\text{NO}_3^-$       d.  $\text{C}_2\text{O}_4^{2-}$

a ii. The confirmation test for Zinc ions results in what color of precipitate?

- a. white      b. black      c. grey      d. yellow

b iii. What pH is required to separate Copper(II) ions from Zinc ions using a sulfide precipitation?

- a. 0.0      b. 0.5      c. 1.0      d. 1.5

a iv. Thioacetamide is used to perform what kind of precipitation?

- a. sulfide      b. nitride      c. acetamide      d. chloride

b v. Which ion is used as a confirmation of zinc ions?

- a.  $\text{Cl}^-$       b.  $\text{K}_4\text{Fe}(\text{CN})_6$       c.  $\text{NO}_3^-$       d.  $\text{C}_2\text{O}_4^{2-}$

B. Solid Unknowns

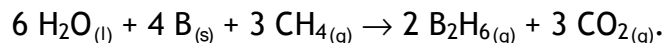
You receive a solid unknown. You dissolve the unknown into water and perform the tests we do in lab. You get the following results:

- The unknown does not precipitate with  $\text{Sr}^{2+}$  but does precipitate with  $\text{Ag}^+$ . **This leaves  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{C}_2\text{H}_3\text{O}_2^-$**
- There is no detectable reaction with  $\text{MnO}_4^-$ . **This leaves only  $\text{C}_2\text{H}_3\text{O}_2^-$**
- Addition of aqueous ammonia results in a light colored precipitate that does not react with  $\text{H}_2\text{O}_2$ . **This means it's not  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Cu}^{2+}$**
- The precipitate does dissolve with the addition of acid but does not react with KSCN. **Again, not  $\text{Fe}^{3+}$**
- The unknown does precipitate with thioacetamide at high pH. The precipitate dissolves in acid and precipitates with  $\text{K}_4\text{Fe}(\text{CN})_6$  as a white precipitate. **This is indicative of  $\text{Zn}^{2+}$ . It cannot be  $\text{Ag}^+$  because the substance precipitates with  $\text{Ag}^+$  in the first result.**

The solid you were given is: Name **Zinc Acetate**

Formula  **$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$**

8. The following reaction is carried out in a bomb calorimeter:



The calorimeter has a heat capacity of  $16.31 \text{ kJ } ^\circ\text{C}^{-1}$ .  $15.43 \text{ g}$  of boron reacts with a large excess of methane ( $\text{CH}_4$ ) in the calorimeter and the temperature increases from  $18.40^\circ\text{C}$  to  $23.51^\circ\text{C}$ .

a. Calculate the *molar internal energy change* for this reaction.

$$q_{cal} = C\Delta T = (16.31 \text{ kJ } ^\circ\text{C}^{-1})(23.51^\circ\text{C} - 18.40^\circ\text{C}) = 83.3441 \text{ kJ} = -q_{rxn}$$

$$\Delta U = \frac{q_{rxn}}{n} = \frac{-83.3441 \text{ kJ}}{15.43 \text{ g B}} \times \frac{10.811 \text{ g B}}{1 \text{ mol B}} \times \frac{4 \text{ mol B}}{1 \text{ mol rxn}} = -233.57954 \text{ kJ mol}^{-1}$$
$$= -233 \text{ kJ mol}^{-1}$$

b. Calculate the *molar enthalpy change* for this reaction.

$$\Delta H = \Delta U + \Delta nRT = -233.57954 \text{ kJ mol}^{-1} + \left( \frac{2 \text{ mol gas}}{\text{mol rxn}} \right) \left( \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mol gas K}} \right) (298.15 \text{ K})$$
$$= -228.6219 \text{ kJ mol}^{-1} = -229 \text{ kJ mol}^{-1}$$