

1. Calculate the *temperature, in °C*, at which Dinitrogen Tetroxide decomposes into Nitrogen Dioxide. You have the following thermodynamic data to use as you see fit:

Compound	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol-K)
Dinitrogen Tetroxide	9.08	304.38
Nitrogen Dioxide	33.1	240.03



$$\Delta H_{rxn}^\circ = \left[ \left( \frac{2 \text{ mol NO}}{\text{mol rxn}} \right) \left( 33.1 \frac{\text{kJ}}{\text{mol NO}} \right) \right] - \left[ \left( \frac{1 \text{ mol N}_2\text{O}_4}{\text{mol rxn}} \right) \left( \frac{9.08 \text{ kJ}}{\text{mol N}_2\text{O}_4} \right) \right] = 57.12 \text{ kJ/mol rxn}$$

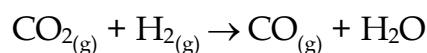
$$\Delta S_{rxn}^\circ = \left[ \left( \frac{2 \text{ mol NO}}{\text{mol rxn}} \right) \left( 240.03 \frac{\text{J}}{\text{mol NO K}} \right) \right] - \left[ \left( \frac{1 \text{ mol N}_2\text{O}_4}{\text{mol rxn}} \right) \left( \frac{304.38 \text{ J}}{\text{mol N}_2\text{O}_4 \text{ K}} \right) \right] = 175.68 \text{ J/mol rxn K}$$

$$\Delta G = 0 > \Delta H_{rxn}^\circ - T \Delta S_{rxn}^\circ$$

$$T \Delta S_{rxn}^\circ > \Delta H_{rxn}^\circ$$

$$T > \frac{\Delta H_{rxn}^\circ}{\Delta S_{rxn}^\circ} = \frac{57.12 \times 10^3 \text{ J/mol rxn}}{175.68 \text{ J/mol rxn K}} = 325.1 \text{ K} = 52.0 \text{ }^\circ\text{C}$$

2. The reaction



is nonspontaneous at room temperature but becomes spontaneous at a much higher temperature. What can you conclude from this about the sign of  $\Delta H^\circ$  and  $\Delta S^\circ$ , assuming that the enthalpy and entropy changes are not greatly affected by the temperature change? Explain your reasoning.

If  $\Delta G$  is negative at higher temperatures but positive lower temperatures it means that  $\Delta S^\circ$  and  $\Delta H^\circ$  must both be positive. When the temperature increases the  $T\Delta S^\circ$  term overwhelms the  $\Delta H^\circ$  term making  $\Delta G$  become negative.

3. A bumper has a surface area of 1524 cm<sup>2</sup>. You wish to plate it with Chromium starting with Chromium(III) Chloride. The thickness of the plating must be 0.025 cm. How much *current* should you use so that the bumper is plated in 15.0 hours? The density of Chromium is 7.14 g/cm<sup>3</sup>.

$$? \frac{\text{C}}{\text{s}} = \frac{(1524 \text{ cm}^2)(0.025 \text{ cm})}{15.0 \text{ h}} \times \frac{7.14 \text{ g Cr}}{1 \text{ cm}^3} \times \frac{1 \text{ mol Cr}}{51.996 \text{ g Cr}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ amp}}{1 \text{ C s}^{-1}} = 28 \text{ amp}$$

4. Using the information from problem 1, calculate the total pressure and the partial pressure of Nitrogen Dioxide at equilibrium at 60.0°C when the reaction starts with 1.00 atm of Dinitrogen Tetroxide at 60.0°C.

$$\Delta H_{rxn}^{\circ} = \left[ \left( \frac{2 \text{ mol NO}}{\text{mol rxn}} \right) \left( 33.1 \frac{\text{kJ}}{\text{mol NO}} \right) \right] - \left[ \left( \frac{1 \text{ mol N}_2\text{O}_4}{\text{mol rxn}} \right) \left( \frac{9.08 \text{ kJ}}{\text{mol N}_2\text{O}_4} \right) \right] = 57.12 \text{ kJ/mol rxn}$$

$$\Delta S_{rxn}^{\circ} = \left[ \left( \frac{2 \text{ mol NO}}{\text{mol rxn}} \right) \left( 240.03 \frac{\text{J}}{\text{mol NO K}} \right) \right] - \left[ \left( \frac{1 \text{ mol N}_2\text{O}_4}{\text{mol rxn}} \right) \left( \frac{304.38 \text{ J}}{\text{mol N}_2\text{O}_4 \text{ K}} \right) \right] = 175.68 \text{ J/mol rxn K}$$

$$\Delta G = \Delta H_{rxn}^{\circ} - T \Delta S_{rxn}^{\circ}$$

$$= \left( 57.12 \times 10^3 \frac{\text{J}}{\text{mol rxn}} \right) - (333.2 \text{ K}) \left( 175.68 \frac{\text{J}}{\text{mol rxn K}} \right) = -1416.58 \text{ J/mol rxn}$$

$$K = e^{-\Delta G / RT} = e^{-(-1416.58 \text{ J/mol}) / (8.314 \text{ J/mol K}) (333.2 \text{ K})} = 1.668$$

Set up equilibrium calculation:

	$\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$	
I	1.00	0
C	-x	+2x
E	1.00-x	2x

$$K_{eq} = K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 1.668 = \frac{(2x)^2}{(1.00 - x)}$$

$$1.668 - 1.668x = 4x^2$$

$$4x^2 + 1.668x - 1.668 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.668) \pm \sqrt{(1.668)^2 - 4(-1.668)}}{2(4)} = 0.47008 \text{ or } -0.88708$$

We choose the value that makes sense, 0.470. This gives a total pressure of:

$$P_T = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2} = (1.00 \text{ atm} - x) + 2x = 1.00 \text{ atm} + x = 1.47 \text{ atm}$$

The partial pressure of  $\text{NO}_2$  at equilibrium is:

$$P_{\text{NO}_2} = 2x = 2(0.470 \text{ atm}) = 0.940 \text{ atm}$$

5. Give 1 test (and **ONLY** 1 test) to determine which ion in the following pairs is present. State what results would be expected for each ion in that test. No points if more than one test is given.

(a)  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$

Adding Strontium ion will determine which is present. If  $\text{Cl}^-$ , there will be no ppt. If  $\text{SO}_4^{2-}$ , there will be a white ppt.

(b)  $\text{Fe}^{3+}$  and  $\text{Ag}^+$

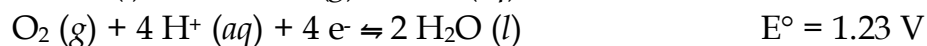
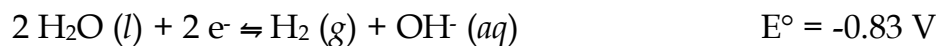
Adding HCl will do it. If  $\text{Fe}^{3+}$ , there will be no ppt. If  $\text{Ag}^+$ , there will be a white ppt.

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

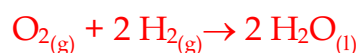
A white precipitate forms under slightly basic conditions when Strontium Nitrate is added. A white precipitate forms with the addition of Silver Nitrate. Addition of Potassium Permanganate and extraction with cyclohexane gives a dark purple aqueous layer and a colorless organic layer. Flame tests give 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 is  **$\text{CuSO}_4$  - Copper(II) Sulfate**  
(give the **name** and **formula**)

7. (a) Calculate the equilibrium constant for the fuel cell reaction used in the Apollo space missions. The cell consisted of the following half-reactions:



The overall equation is:



with a transfer of 4 electrons.

$$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}} = 1.23 \text{ V} - (-0.83 \text{ V}) = 2.06 \text{ V}$$

$$K = e^{nFE_{\text{cell}}/RT} = e^{\left( \frac{(4 \text{ mol } e^-)(96485 \text{ C mol}^{-1})(2.06 \text{ V})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} \right)} = e^{320.73} = 1.95 \times 10^{139} \approx 10^{139}$$

- (b) If the pressure of Hydrogen gas is 1.50 atm and the pressure of Oxygen gas is 10.00 atm at 600.0 K, what is the potential given by this cell?

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln \frac{1}{P_{\text{O}_2} P_{\text{H}_2}^2} \\ &= 2.06 \text{ V} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(600.0 \text{ K})}{\left( \frac{4 \text{ mol } e^-}{\text{mol}} \right) \left( \frac{96485 \text{ C}}{\text{mol } e^-} \right)} \ln \left[ \frac{1}{(10.00)(1.50)^2} \right] \\ &= 2.10 \text{ V} \end{aligned}$$