

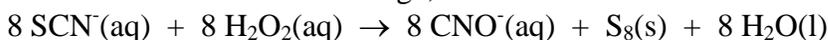
A periodic table with useful constants is provided as an insert. You may use the back for scratch work but enter all work to be graded in the space provided with each question.

1) (35 points) The thiocyanate anion, SCN^- , was once one of the anions in the Five Anion Experiment. It is oxidized in an aqueous, **acidic** solution of hydrogen peroxide to form the cyanate anion, CNO^- , and sulfur as S_8 . **Using the method of half reactions**, write a balanced, net-ionic equation for this reaction.



The second, reduction half reaction should be familiar because of the lab.

To balance the transfer of charge, combine $1 \times \text{O} + 8 \times \text{R}$ and simplify.



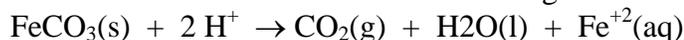
2) (25 points) Military missiles and the rocket for the space shuttle are now propelled by a highly exothermic solid-state reaction. The launch vehicles are filled with a mixture of powdered aluminum and ammonium perchlorate. What class of reaction is employed here? Why is the reaction so exothermic? Hint: perchlorate is ClO_4^- .

The mixture contains two strong reducing agents: aluminum metal and the ammonium ion. Metals are good reducing agents; aluminum's high electrical conductivity suggests this. Nitrogen in the ammonium ion has an oxidation number of -3, the minimum value possible for this element. Chlorine in perchlorate has an oxidation number of +7; this is maximum possible for chloride and perchlorate is a very strong oxidizing agent. The combination of strong reducing and oxidizing agents results in a redox reaction with a strong forward drive. The mixture is kinetically inert until detonation of a fuse at ignition initiates the reaction.

3) (50 points) Write balanced, net-ionic equations for the reactions that occur when the following pairs of aqueous solutions or slurries are mixed.

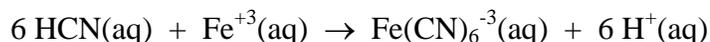
a) siderite [iron(II) carbonate] and hydrochloric acid

Siderite is water insoluble. HCl is a strong acid.

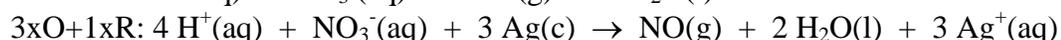
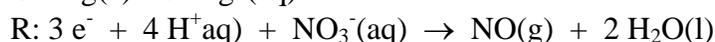
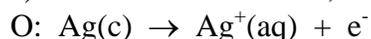


b) iron(III) nitrate and hydrocyanic acid [HCN]

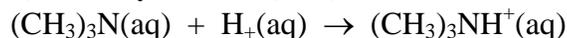
HCN is a weak acid.



c) metallic silver and hot, 6 M nitric acid



d) trimethylamine [(CH₃)₃N] and cold, dilute nitric acid



4) (25 points) The system in this problem is a box with the following **initial** conditions: a volume V₀ at a temperature T₀. The box is filled with n₀ moles of N₂ at a total pressure of p₀.

a) Determine quantitatively the multiplicative effect, e.g. p(final)/p₀ = 47, on the total pressure in the box as a result of the following changes.

$$\underline{p(\text{final})/p_0}$$

i) the box's volume is doubled and its temperature is tripled 3/2
Doubling V halves p but tripling T increases p by 3. Together, 3 x 1/2 = 3/2.

ii) another n₀ moles of N₂ are added and the volume is halved 4
Adding more N₂ doubles p as does halving V. The 2 effects combine: 2 x 2 = 4.

iii) 4n₀ moles of hydrogen are added and the reaction



p is proportional to the total number of moles of gas irrespective of chemical identity. The checking balance for n is n₀ (start) + 4n₀ (adding H₂) - 4n₀ (reaction of H₂ and N₂) + 2n₀ (production of ammonia) = 3n₀.

b) Suppose that p₀ were very high, e.g. 10 GPa. Could you now easily solve part (a)? Briefly explain.

The answer is NO. Under high pressure, the total volume occupied by the molecules themselves and the short-range forces between molecules become important and the gas no longer obeys pV = nRT. The equation of state becomes complicated.

5) (65 points) A researcher who plans to study the carbon-13 NMR spectroscopy of carbon dioxide prepares a solution of $^{13}\text{CO}_2$ (carbon dioxide in which all carbon atoms are carbon-13) in CDCl_3 .

a) To this end, he dissolves 47 mg of $\text{Na}_2^{13}\text{CO}_3$ in 50 mL of water at 25.0°C , adds a stoichiometric amount of 0.10 M HCl, and collects the gaseous $^{13}\text{CO}_2$ in a 0.500 L flask at 25.0°C .

i) Calculate the total pressure and the partial pressure of carbon dioxide in the flask.

The reaction is $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ so
 $n_{\text{CO}_2} = n_{\text{CO}_3^{2-}} = n_{\text{Na}_2\text{CO}_3} = (0.047 \text{ g}) / (107 \text{ g/mole}) = 4.39 \times 10^{-4} \text{ mole}$
 $M(\text{Na}_2\text{CO}_3) = 1(23) + 1(13) + 3(16) = 107 \text{ g/mole C-13!!}$

$$T(\text{K}) = 25.00 + 273.15 = 298.15 \text{ K}$$

$$\begin{aligned} p_{\text{CO}_2} &= n_{\text{CO}_2}RT/V = \\ &= (4.39 \times 10^{-4} \text{ mole})(0.08206 \text{ L}\cdot\text{atm/mole}\cdot\text{K})(298.15 \text{ K}) / (0.500 \text{ L}) \\ &= 0.0215 \text{ atm} = 760 \times 0.0215 = 16.3 \text{ torr} \end{aligned}$$

$$p_{\text{T}} = p_{\text{CO}_2} + p_{\text{H}_2\text{O}} = 16.3 + 23.8 = 40.1 \text{ torr}$$

ii) Calculate the minimum volume of HCl solution required for the conversion of all the sodium carbonate to carbon dioxide.

$$\begin{aligned} n_{\text{H}^+} &= 2n_{\text{CO}_2} = 2(4.39 \times 10^{-4} \text{ mole}) = 8.78 \times 10^{-4} \text{ mole} \\ V_{\text{H}^+} &= n_{\text{H}^+} / [\text{HCl}] = (8.78 \times 10^{-4} \text{ mole}) / (0.10 \text{ M}) = 8.78 \times 10^{-3} \text{ L} \end{aligned}$$

b) He passes the contents of the flask over to P_2O_5 to remove the water and transfers the dry carbon dioxide to an NMR tube.

i) Why did he use P_2O_5 to dry the gaseous product of the reaction?

Oxides of non-metals in a high oxidation state are acidic oxides that avidly react with water to form a strong acid.

ii) He distills 0.50 mL of CDCl_3 into the NMR tube so that the carbon dioxide dissolves in the CDCl_3 . Calculate the molar concentration of the carbon dioxide in the resulting CDCl_3 solution. The density of CDCl_3 is 1.50 g/cm^3 .

$$[\text{CO}_2] = n_{\text{CO}_2} / V = (4.39 \times 10^{-4} \text{ mole}) / (0.0005 \text{ L}) = 0.89 \text{ M}$$

The small contribution of CO_2 to the volume of the solution is ignored.