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.

O: $8\ H_2O + 8\ SCN^- \rightarrow 8\ CNO^- + S_8 + 16\ H^+ + 16\ e-$
R: 2 e- + 2 H+ + H2O2 $\rightarrow$ 2 H2O
The second, reduction half reaction should be familiar because of the lab.
To balance the transfer of charge, combine 1 x O + 8 x R and simplify.
$8\ SCN^-(aq) + 8\ H_2O_2(aq) \rightarrow 8\ CNO^-(aq) + S_8(s) + 8\ H_2O(l)$

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.
$FeCO_3(s) + 2 H^+ \rightarrow CO_2(g) + H2O(l) + Fe^{+2}(aq)$

b) iron(III) nitrate and hydrocyanic acid [HCN]
HCN is a weak acid.
$6 HCN(aq) + Fe^{+3}(aq) \rightarrow Fe(CN)_6^{-3}(aq) + 6 H^+(aq)$

c) metallic silver and hot, 6 M nitric acid
O: $Ag(c) \rightarrow Ag^+(aq) + e^-$
R: $3 e^- + 4 H^+ aq) + NO_3^-(aq) \rightarrow NO(g) + 2 H_2O(l)$
3xO+1xR: $4 H^+(aq) + NO_3^-(aq) + 3 Ag(c) \rightarrow NO(g) + 2 H_2O(l) + 3 Ag^+(aq)$

d) trimethylamine [$(CH_3)_3N$] and cold, dilute nitric acid
$(CH_3)_3N(aq) + H_+(aq) \rightarrow (CH_3)_3NH^+(aq)$

4) (25 points) The system in this problem is a box with the following **initial** conditions: a volume V_0 at a temperature T_0. The box is filled with n_0 moles of N_2 at a total pressure of p_0.

a) Determine quantitatively the multiplicative effect, e.g. p(final)/p_0 = 47, on the total pressure in the box as a result of the following changes.

p(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 n_0 moles of N_2 are added and the volume is halved ______4________
Adding more N_2 doubles p as does halving V. The 2 effects combine: 2 x 2 = 4.

iii) $4n_0$ moles of hydrogen are added and the reaction
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ goes to completion. ______3__________
p is proportional to the total number of moles of gas irrespective of chemical identity. The checking balance for n is n_0 (start) + $4n_0$ (adding H_2) - $4n_0$ (reaction of H_2 and N_2) + $2n_0$ (production of ammonia) = $3n_0$.

b) Suppose that p_0 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 $^{13}CO_2$ (carbon dioxide in which all carbon atoms are carbon-13) in $CDCl_3$.

a) To this end, he dissolves 47 mg of $Na_2{}^{13}CO_3$ in 50 mL of water at 25.0ºC, adds a stoichiometric amount of 0.10 M HCl, and collects the gaseous $^{13}CO_2$ in a 0.500 L flask at 25.0ºC.

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

The reaction is $CO_3^{-2}(aq) + 2\ H^+(aq) \rightarrow CO_2(g) + H_2O(l)$ so
$n_{CO2} = n_{CO3\text{-}2} = n_{Na2CO3} = (0.047\ g)/(107\ g/mole) = 4.39 \times 10^{-4}$ mole
$M(Na_2CO_3) = 1(23) + 1(13) + 3(16) = 107$ g/mole C-13!!

T(K) = 25.00 + 273.15 = 298.15 K

$p_{CO2} = n_{CO2}RT/V =$
$= (4.39 \times 10^{-4}\ \text{mole})(0.08206\ \text{L-atm/mole-K})(298.15\ K)/(0.500\ L)$
$= 0.0215\ \text{atm} = 760 \times 0.0215 = 16.3$ torr

$p_T = p_{CO2} + p_{H2O} = 16.3 + 23.8 = 40.1$ torr

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

$n_{H+} = 2n_{CO2} = 2(4.39 \times 10^{-4}\ \text{mole}) = 8.78 \times 10^{-4}$ mole
$V_{H+} = n_{H+}/[HCl] = (8.78 \times 10^{-4}\ \text{mole})/(0.10\ M) = 8.78 \times 10^{-3}$ L

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.

$[CO_2] = nCO2/V = (4.39 \times 10^{-4}\ \text{mole})/(0.0005\ L) = 0.89$ M
The small contribution of CO_2 to the volume of the solution is ignored.