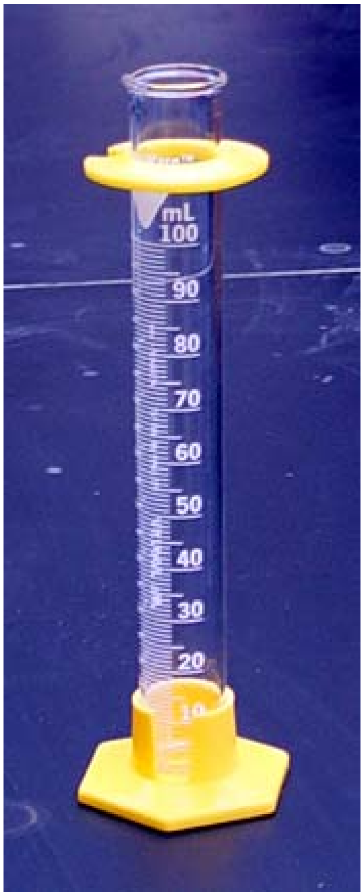
Chapter 10 – Some Elementary Thoughts for Laboratory Techniques and Supplies in Qualitative Chemical Analysis	**NAME:**	
	Lab Section:	
	Date:	**Sign-Off:**

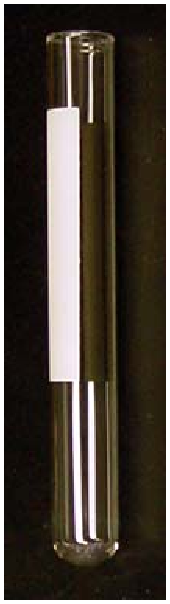
Chapter 10 – Some Elementary Thoughts for Laboratory Techniques and Supplies in Qualitative Chemical Analysis

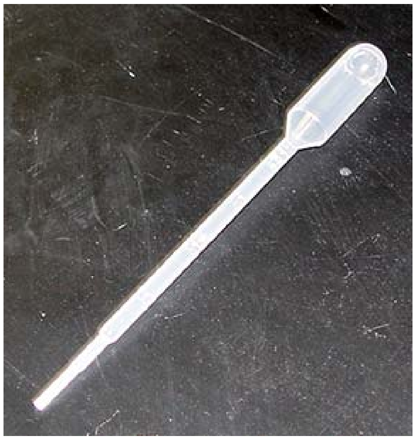
There are many pieces of glassware that are used in Qualitative Chemical Analysis, such as a 100 mL graduated cylinder, figure right, or a 10 mL graduated cylinder, below left:



In addition, there are semi-micro spatulas and stirring rods with rubber policeman:

There are also test tube racks, disposable test tubes and disposable pipets that are utilized across chemistry lab courses:





And beakers, flasks and goggles are important, too:

Centrifuges are used, as well (open and closed images, below):

Parafilm, used for inverting samples to mix, and a vortex, used to mix liquid samples in an upright vertical position, are important, as well:

There are some pieces of ceramic wear that are unique to qualitative analysis. That includes spot plates and casseroles – these are used for rapid detection on solid samples and for “cooking down” minute volumes of solutions, respectively:

Terminology

Because qualitative analysis is a study of “what” is present and not “how much” of a substance is present in something, there are a few terminology phrases with which you need to become familiar.

“Few”: means 1-2, e.g., add a few drops of some reagent means 1-2 drops of the reagent are added.

“Several”: means 2-4, e.g., add several drops of some reagent means 2-4 drops of the reagent are added.

“Dissolve in a minimum of water”: when adding water to a solid salt, add it a drop or two at a time with mixing until you just get it dissolved, i.e., you didn’t use an excess of water.

“Make the solution acidic or alkaline to litmus”: add a drop of the proper reagent to the solution under study, mix with a stirring rod being careful to not knock the bottom of the tube out, then touching the wet end of the rod to the litmus paper to see if it turns the proper color – repeat as necessary. This prevents using too much indicator paper in a wasteful manner and minimizes the risk to you of getting an acid or base burn on your skin.

“One drop in excess”: add the reagent until the desired response has occurred, then add one more drop and add no more unless there are instructions to go beyond that amount.

When adding liquid reagents, do not touch the side of the tube with the pipet – better to drop the reagents a drop at a time into the tube – the exception is when adding concentrated acids to an aqueous solution and that will be covered by your professor.

When labeling your test tubes, remember that they can be written on with pencil in the white paint spot – the graphite will not come off – this is one exception to using ink in the chemistry lab. Labeling the tubes will make your life much easier and more organized – label them ahead of time so you can flow right into them.

Keeping your lab bench clean and your glass ware clean is of great importance in qual – even a small amount of contaminant will mess up your work and cause great wailing and gnashing of teeth – particularly when you’ve spent 6 weeks working on an experiment and have to start over.

Notes must be kept – even if they are written NEATLY in the margin of your experiment, they **must** be written as you go along – do not trust your memory to remember them until the next week – won’t happen. Write them in your book in ink – if you err, run a single line through the error, initial and date the error and go on. Do not write your notes on a paper towel, then transfer them into your book after lab—lab time is set up so that you have the time to record your notes right then.

It is also of the utmost importance that you prepare a rough outline of the work to be done before you come into lab – this will save you many hours of frustration and keep you on schedule in the lab. While you’ll have to refer to your book for the actual preps, the outline will speed it up for you in finding it.

Remember that you are studying the most exciting field in chemistry there is: you’re performing experiments that are founded in some of the most exquisite mathematics that explains how inorganic chemistry works – and your mind is learning a whole new manner in which to solve problems rationally and logically – without any use of intuition or speculation. What an amazing journey you are undertaking!

Chapter 11 – Reagents Necessary for Qualitative Analysis by Group

NAME:

Lab Section:

Date: **Sign-Off:**

Chapter 11 – Reagents Necessary for Qualitative Analysis by Group

Anion Analysis

Solid Sodium Nitrate – in bottle.

Devarda's Alloy – in bottle.

Solid Ferrous Sulfate Heptahydrate – in bottle.

Concentrated Sulfuric Acid – in bottle.

Solid Sodium Nitrite – in bottle.

Solid Sodium Sulfide – in bottle.

4 or 6 or 8M Sulfuric Acid – Concentrated sulfuric acid is approximately 18M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Sulfuric acid is particularly dangerous in that it will boil and spatter on you if not done correctly. Wear goggles and work in the hood when doing this. To prepare 500 mL of 4M sulfuric acid, dilute 111 mL con sulfuric to a final volume of 500 mL. To prepare 500 mL of 6M sulfuric acid, dilute 167 mL con sulfuric to a final volume of 500 mL. To prepare 500 mL of 8M sulfuric acid, dilute 222 mL con sulfuric acid to a final volume of 500 mL.

Lead Acetate Paper – prepared for you in lab.

6M Hydrochloric Acid – Concentrated hydrochloric acid is approximately 12 M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M HCl, dilute 250 mL con HCl with enough water to make a final volume of 500 mL.

1M Barium Chloride – 244 g of barium chloride dihydrate dissolved in one liter of water.

Solid Trisodium Phosphate Dodecahydrate – in bottle.

6M Nitric Acid -- Concentrated nitric acid is approximately 15 M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M nitric acid, dilute 200 mL con nitric acid with enough water to make a final volume of 500 mL.

Magnesia Mixture – dissolve 130 g magnesium nitrate hexahydrate and 240 g ammonium nitrate in 500 mL distilled water. Add 150 mL con ammonia (15 M) and dilute to 1 liter.

Solid Sodium Carbonate – in bottle.

Concentrated Ammonia – in bottle – is 15M.

0.2 M Barium Chloride – 48.8 g of barium chloride dihydrate dissolved in one liter of water.

Group 1 Analysis

6M Hydrochloric Acid -- Concentrated hydrochloric acid is approximately 12 M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M HCl, dilute 250 mL con HCl with enough water to make a final volume of 500 mL.

0.5M Potassium Chromate – dissolve 97.1 g of potassium chromate in 1 liter of distilled water.

Concentrated Ammonia – in bottle – 15M.

6M Nitric Acid -- Concentrated nitric acid is approximately 15 M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M nitric acid, dilute 200 mL con nitric acid with enough water to make a final volume of 500 mL.

Group 2 Analysis

Red Litmus Paper – in bottle on lab bench.

6M Ammonia – dilute 200 mL con ammonia with enough water to make 500 mL of solution.

2M Hydrochloric Acid – Concentrated hydrochloric acid is approximately 12 M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 2 M HCl dilute 83.3 mL con HCl with enough distilled water to make 500 mL.

Wide Range pH Paper – on bench in bottle.

Thioacetamide – dissolve 130 g TA in 1 liter of distilled water. After a year, test with barium chloride – if there is a ppt, re-make.

0.5M Potassium Hydroxide – dissolve 28 g with stirring in 1 liter of distilled water. This is caustic – lye's big brother.

Clorox – from the store in the bottle.

Tin Chloride Solution – let 45 g stannous chloride dehydrate stand in 170 mL con HCl until disintegrated. Decant slowly and carefully into enough distilled water to make a final volume of 1 liter. Keep tin shot in the solution.

Concentrated Sulfuric Acid – in bottle – approximately 18M – probably the most dangerous acid you'll use in the chem lab at WNCC – wear goggles.

Ammonium Acetate – to prepare a liter of a 3M solution, dissolve 231.2 g in 1 liter of distilled water.

6M Acetic Acid -- Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M HOAc, dilute 176.5 mL glacial HOAc with enough water to make a final volume of 500 mL.

0.5M Potassium Chromate -- dissolve 97.1 g of potassium chromate in 1 liter of distilled water.

Sodium Stannite Solution – to one drop (1 gtt) of stannous chloride reagent, add 6M NaOH drop-by-drop until the ppt re-dissolves. Use soon.

6M Sodium Hydroxide – dissolve 240 g of NaOH in 1 liter of distilled water in the hood, with stirring, with the hood on. This solvation is exothermic and gives off caustic fumes – do NOT breathe.

Group 3 nalysis

6M Ammonium Chloride – dissolve 320 g ammonium chloride in 1 liter of water.

Concentrated Ammonia – 15M in bottle.

Red Litmus Paper – in bottle on bench.

Thioacetamide -- dissolve 130 g TA in 1 liter of distilled water. After a year, test with barium chloride – if there is a ppt, re-make.

Solid Ammonium Nitrate – in bottle.

6M Hydrochloric Acid -- Concentrated hydrochloric acid is approximately 12 M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M HCl, dilute 250 mL con HCl with enough water to make a final volume of 500 mL.

6M Nitric Acid -- Concentrated nitric acid is approximately 15 M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M nitric acid, dilute 200 mL con nitric acid with enough water to make a final volume of 500 mL.

Aqua Regia – mix 1 part con nitric acid with 3 parts con HCl in the hood. Use as you make it.

Dimethylglyoxime – dissolve 10 g DMG in 1 liter of 95% ethanol.

Hydrogen Peroxide – 3% in bottle.

6M Sodium Hydroxide -- dissolve 240 g of NaOH in 1 liter of distilled water in the hood, with stirring, with the hood on. This solvation is exothermic and gives off caustic fumes – do NOT breathe.

6M Sulfuric Acid -- Concentrated sulfuric acid is approximately 18M in the bottle. Remember that when diluting acids to decant the acid carefully into the water. Sulfuric acid is particularly dangerous in that it will boil and spatter on you if not done correctly. Wear goggles and work in the hood when doing this. To prepare 500 mL of 6M sulfuric acid, dilute 167 mL con sulfuric to a final volume of 500 mL.

Potassium Thiocyanate – solid in bottle.

6M Ammonia -- dilute 200 mL con ammonia with enough water to make 500 mL of solution.

Aluminon Reagent – dissolve 1 g of the ammonium salt of aurintricarboxylic acid in a liter of distilled water.

Diphenylthiocarbazone Paper – in bottle on bench.

Group 4 Analysis

Concentrated Ammonia – 15M in bottle.

3M Ammonium Carbonate – dissolve 288 g of solid ammonium carbonate in 500 mL of distilled weater and 80 mL con ammonia. Dilute to 1 Liter.

Reagent Alcohol – in bottle in lab.

6M Acetic Acid -- Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M HOAc, dilute 176.5 mL glacial HOAc with enough water to make a final volume of 500 mL.

3M Ammonium Acetate – dissolve 231.2 g in 1 liter of distilled water.

0.5M Potassium Chromate – dissolve 97.1 g in 1 liter of distilled water.

0.5 M Ammonium Sulfate – dissolve 66 g solid ammonium sulfate in 1 liter of distilled water.

0.25M Ammonium Oxalate – dissolve 28.4 g ammonium oxalate monohydrate in 1 liter of distilled water.

Group 5 Analysis

0.5M Ammonium Sulfate -- dissolve 66 g solid ammonium sulfate in 1 liter of distilled water.

0.25M Ammonium Oxalate -- dissolve 28.4 g ammonium oxalate monohydrate in 1 liter of distilled water.

Concentrated Ammonia – 15M in bottle.

0.5M Disodium Hydrogen Phosphate – dissolve 71 g of the anhydrous salt a bit at a time in 1 liter of distilled water with constant stirring.

6M Acetic Acid -- Remember that when diluting acids to decant the acid carefully into the water. Wear goggles and work in the hood when doing this. To prepare 500 mL 6 M HOAc, dilute 176.5 mL glacial HOAc with enough water to make a final volume of 500 mL.

References/Bibliography/Citations

King, E.J.: **Qualitative Analysis and Electrolytic Solutions.** (Harcourt, Brace and World, Inc: New York) © 1959.

Weast, R.C. and Astle, M.J., Eds: **CRC Handbook of Chemistry and Physics, 63d Ed.** (CRC Press, Inc.: Boca Raton) ©1982.

Chapter 12 – The Analysis of A Solution for Specific Anions: NO_3^{-1}, NO_2^{-1}, S^{2-}, CO_3^{2-}, PO_4^{3-} and SO_4^{2-}

NAME:

Lab Section:

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Chapter 12 – The Analysis of A Solution for Specific Anions: NO_3^{-1}, NO_2^{-1}, S^{2-}, CO_3^{2-}, PO_4^{3-} and SO_4^{2-}

Introduction

The separation and identification of the halogens have already been examined in an earlier chapter. This chapter deals with anions that are polyatomic and include carbon, nitrogen, phosphorous, and sulfur.

Carbon and Its Compounds

Occurrence: Carbon is 19th among elements in abundance, making up ~ 0.027% of the earth's crust. Diamond and graphite are elemental carbon. Other carbon containing compounds include natural gas (CH_4), petroleum (hydrocarbons, kerosene, oil, gasoline), coal, plants/animals, limestone ($CaCO_3$), dolomite, coral and sponges, chalk – and is in the air as CO_2.

Chemical Properties: almost chemically inert toward most reagents at ordinary temperatures:

$$\text{Graphite} + HNO_3 + NaClO_2 \rightarrow \text{slow oxidation}$$

$$\text{Charcoal} + HNO_3 + NaClO_2 \rightarrow \text{rapid oxidation}$$

The activity of carbon increases rapidly with increasing temperature; at high temps, C reacts with O:

$$C + O_2 \rightarrow 2CO,$$

OR,

depending on the concentration of oxygen around, may form CO_2.

$$C + 2S \rightarrow CS_2;$$

$$3Fe + C \rightarrow Fe_3C \text{ (Iron carbide)};$$

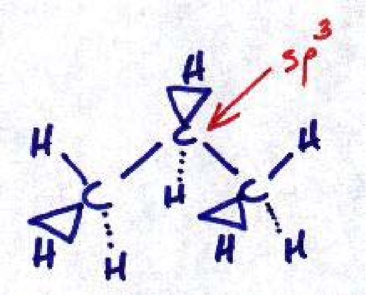
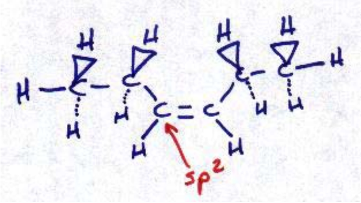
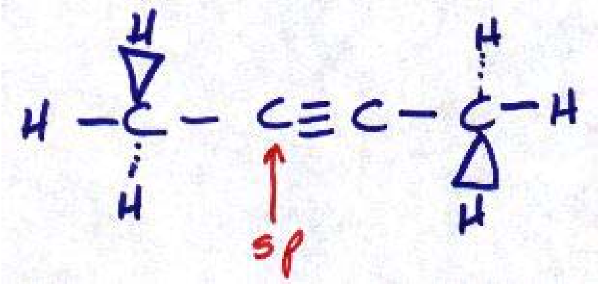
$$C + 2F_2 \rightarrow CF_2;$$

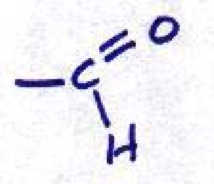
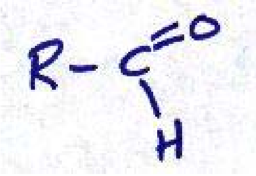
$$\text{Hot } C + 2H_2 + \text{catalyst} \rightarrow CH_4 \text{ (methane)};$$

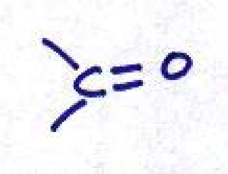
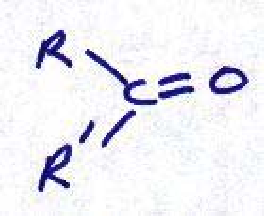
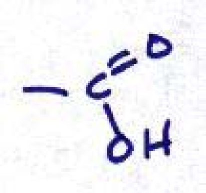
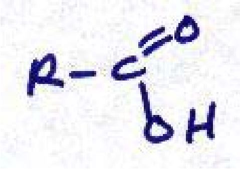
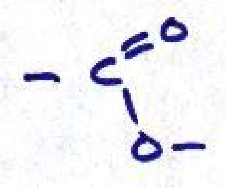
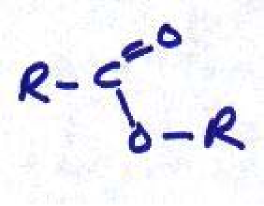
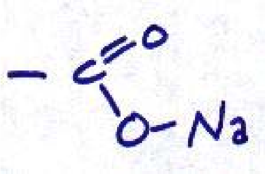
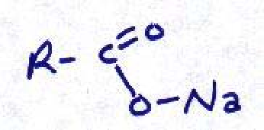
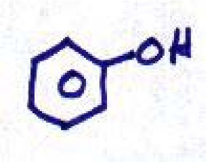
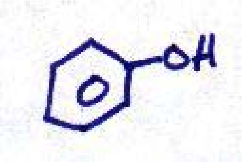
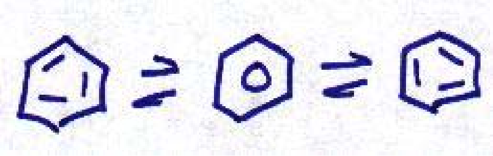
$$2 \text{ Hot } C + H_2 + \text{catalyst} \rightarrow C_2H_2 \text{ (acetylene;}$$

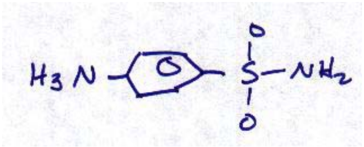
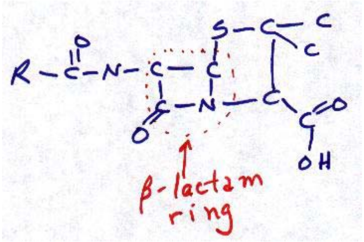
for each of these last two reactions, the yields are very low)

Carbon Compounds

Alkanes	Alkenes	Alkynes
Single C-C bonds	Double C=C bonds	Triple C≡C bonds
C in sp^3	C in sp^2	C in sp
Tetrahedral	Trigonal planar	Linear
		
C-C-C	C-C-C=C-C-C	C-C≡C-C

Hydrocarbon derivatives			
Type	Functional Group	Formula Type	Example
Alcohols	$-OH$	$R-OH$	Methanol
Ethers	$-O-$	$R-O-R'$	Diethyl ether
Aldehydes	 $-C(=O)H$	 $R-C(=O)H$	Formaldehyde

Ketones			Acetone
Acids			Acetic acid
Esters			Ethyl acetate
Salts			Sodium acetate
Phenols			Phenol
Aromatics			Resonant Structures

Medical Agents		
Sulfa drugs		Sulfanilamide
Penicillins		β-lactam ring

Other C Compounds

Carbon dioxide comes from carbonates, carbohydrate fermentation by yeast and from burning hydrocarbons.

Carbonic acid and the bicarbonate ion are the acid-base pair involved in blood gas regulation.

Carbon monoxide (CO) binds to hemoglobin 200X > than does oxygen.

CCl_4 used to be used for dry cleaning and in fire extinguishers (not any more, though):

$$CCl_4 + O_2 + \text{fire} \rightarrow COCl_2 \text{ (phosgene gas)}$$

It was because of the phosgene gas that formed when used to extinguish fires that carbon tet was removed as a fire extinguishing agent.

Carbon: More Applications

COKE	CARBON BLACK	ACTIVATED CARBON
When soft coal is heated at 1100° C in the presence of no oxygen, water, coal tar, hydrogen, carbon monoxide and dioxide, hydrogen sulfide, ammonia, nitrogen, methane and COKE are obtained. Coke is used in blast furnaces as a reducing agent and as fuel.	When petroleum compounds are heated to between 1400° C and 1650° C with oxygen present, carbon black is obtained. Carbon black is used in tires, black inks, paints and plastics as pigments. Carbon black is also used to synthesize graphite (91% of graphite is carbon black). Due to a shortage of natural graphite, the US makes artificial graphite as follows: $SiO_2 + 3C + 2500° C \rightarrow SiC (s) + 2CO$ $SiC + 2500° C \rightarrow Si(g) + C(s)$ The C(s) is the graphite. Graphite is used mainly for electrodes; used to strengthen plastics, as well. It is used to make synthetic "diamonds" (105 atm;>> 2000° C; requires a catalyst like Cr (l), Fe(l), Ni(l) or Pt(l). These "diamonds" are used for drill points, glass cutters and diamond saws.	When carbon is heated to release adsorbed hydrocarbons, activated carbon (charcoal) is obtained. Activated charcoal has an incredible surface area: 5 pounds (approx. 2.5 kg) has about one square mile of surface area. Activated charcoal is used to purify solutions of sugars, remove tastes/odors from water, in gas masks and in air conditioning systems.

Carbon monoxide (CO)

CO is NOT acidic like most non-metal oxides. It forms complexes, e.g.,

$$Ni + 4CO \rightarrow Ni(CO)_4 \text{ (tetracarbonyl nickel(0))}$$

CO is detected by its ability to reduce $PdCl_2$ in solution:

$$CO(g) + PdCl_2(aq) + H_2O \rightarrow Pd(s) + CO_2\uparrow + 2HCl(aq)$$

CO is used for reducing agents for extracting metals from ores:

$$Fe_2O_3(l) + 3CO(g) + heat \rightarrow 2Fe(l) + 3CO_2\uparrow$$

Carbon Dioxide (CO_2)

CO_2 is formed from combustion of hydrocarbons in excess air:

$$CH_4(g) + 2O_2(g) + \text{flame} \rightarrow CO_2\uparrow + 2H_2O(l)$$

$$2CH_3OH(L) + 3O_2(g) + \text{flame} \rightarrow 2CO_2\uparrow + 4H_2O(l)$$

In the lab, CO_2 is produced as follows:

$$CaCO_3(s) + 2H^+ + 2Cl^- \rightarrow CO_2\uparrow + H_2O(l) + Ca^{2+} + 2Cl^-$$

In industry, CO_2 is produced as a by-product of NH_3 synthesis in a 2-step process:

$$1)\ CH_4(g) + 2H_2O(g) + \text{catalyst} \rightarrow CO_2\uparrow + 4H_2\uparrow$$

$$2)\ CO(g) + H_2O(g) + \text{catalyst} + 200\text{-}400^\circ\ C \rightarrow H_2\uparrow + CO_2\uparrow$$

The hydrogen obtained in either reaction is reacted with N_2 to form ammonia.

CO_2 produced by the above methods may be "trapped" as follows:

$$Na_2CO_3(aq) + CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(aq) \text{ plus Energy.}$$

The biological production of carbon dioxide occurs as a fermentative process using sugars:

$$C_6H_{12}O_6\ (aq) + \text{Yeast} + \text{anaerobic conditions} \rightarrow 2\text{Ethyl alcohol} + 2CO_2\uparrow$$

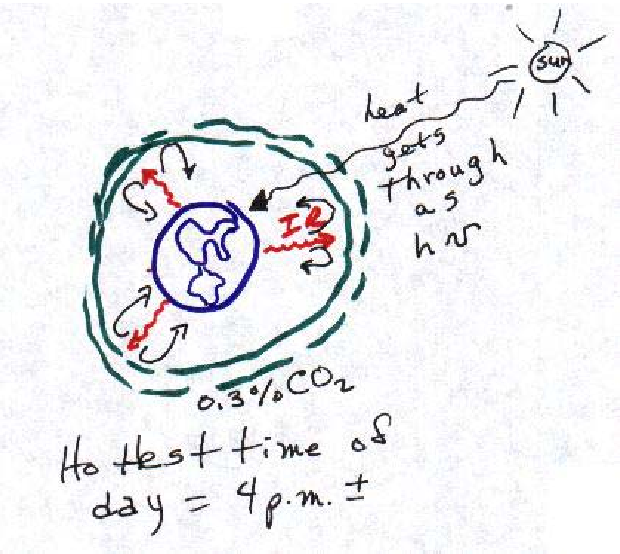
CO_2 does not absorb visible light and it "reflects" infra-red light:

As the percent of CO_2 increases, it may lead to the greenhouse effect, i.e., as CO_2 levels increase, it may warm up the earth and melt the polar caps.

CO_2 may be obtained from the heated degradation/decomposition of limestone:

$$CaCO_3(s) + \text{heat} \rightarrow CaO(s) + CO_2(g)$$

Or of trona ($Na_2CO_3\cdot NaHCO_3\cdot 2H_2O$) from Wyoming:



$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O + \text{heat} \rightarrow 3Na_2CO_3(s) + 5H_2O + CO_2\uparrow$$

CO_2 is used to make baking soda:

$$Na_2CO_3(\text{sat'd}) + H_20(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$$

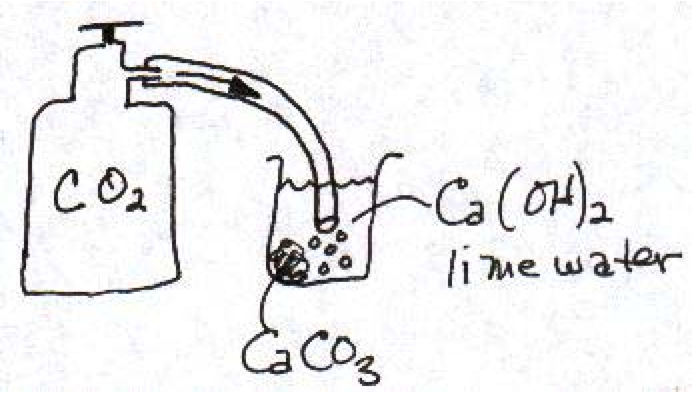
Properties of CO_2

CO_2 is fairly soluble in water (more soluble in cold water like in cold soda; less soluble in warm water like in "flat" soda). A saturated solution at 1 atm and 25° C is approximately 0.033M. At equilibrium only 0.17% of dissolved CO_2 is in the form of carbonic acid (H_2CO_3). An aqueous solution of CO_2 is typically acidic:

$$CO_2(g) + H_2O(l) \rightarrow H^+ + HCO_3^-$$

(Remember the trick with phenolphthalein and blowing into it during titrations in CHEM 121?)

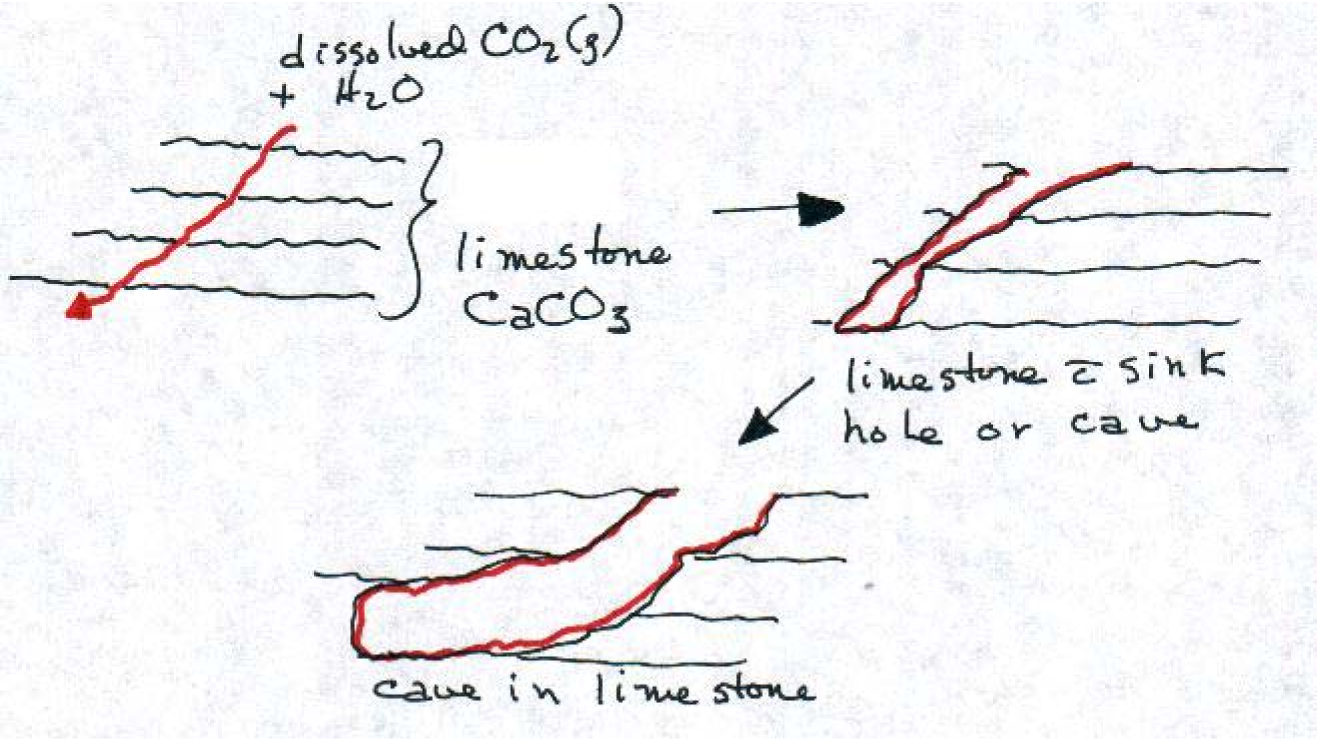
CO_2 reacts with limewater ($Ca(OH)_2$) to form chalk ($CaCO_3$):



CO_2 plays a major role in maintaining the pH of blood and sea water:

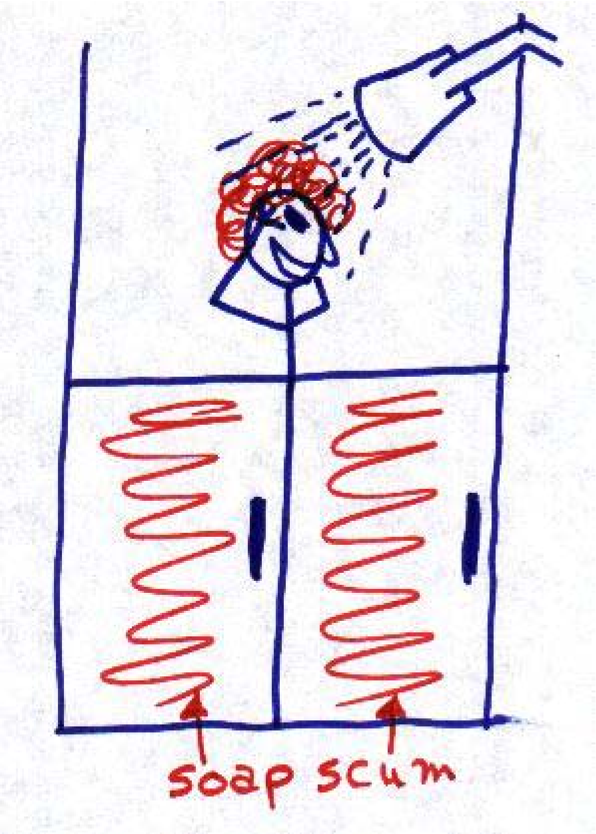
$$H_2O + CO_2 \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

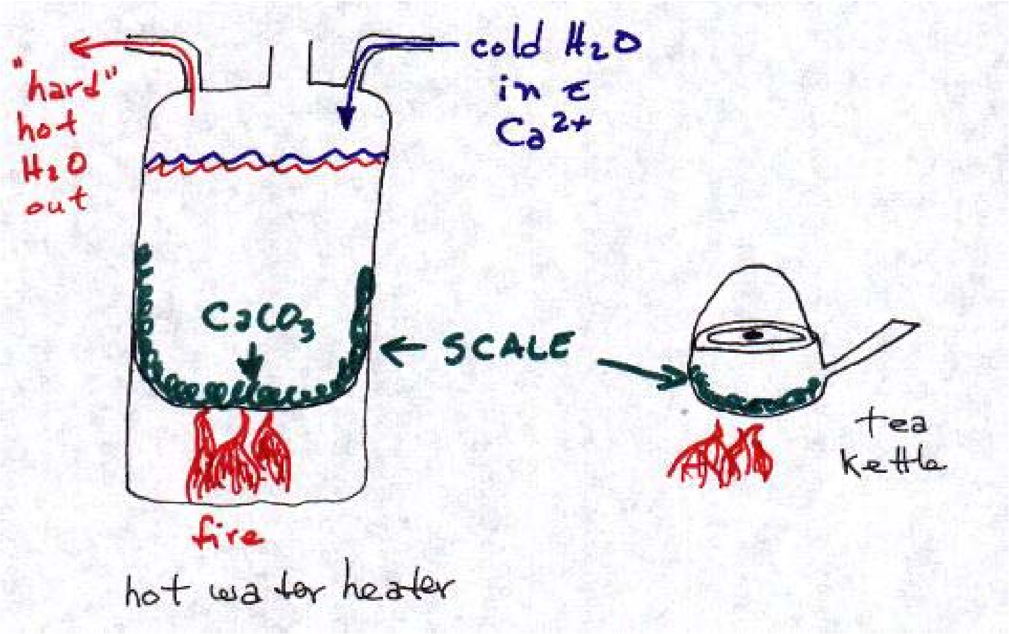
Dissolved CO_2 also plays a role in the formation of caves or sink holes in limestone:



The next three figures all illustrate the significance of ions in water, specifically, carbonate with calcium that makes water "hard".

The water is not hard because you can hit someone with it and hurt them, but "hard" in the sense that it makes it very difficult for soap to lather and suds up. Soap scum (calcium "soapate"), right, builds up on shower surfaces as the soap takes the calcium out of the water, so to speak -- yet, it loses its cleaning power as it removes the calcium from the water. Bicarbonate in the water reacts with calcium to form calcium carbonate (solid) carbon dioxide gas and water. The calcium carbonate is "scale". In boilers, as we discussed in CHEM 121, this scale build-up can lead to boiler explosions. In tea-kettles, next page, top, this scale is relatively harmless as long as one cleans it off regularly.

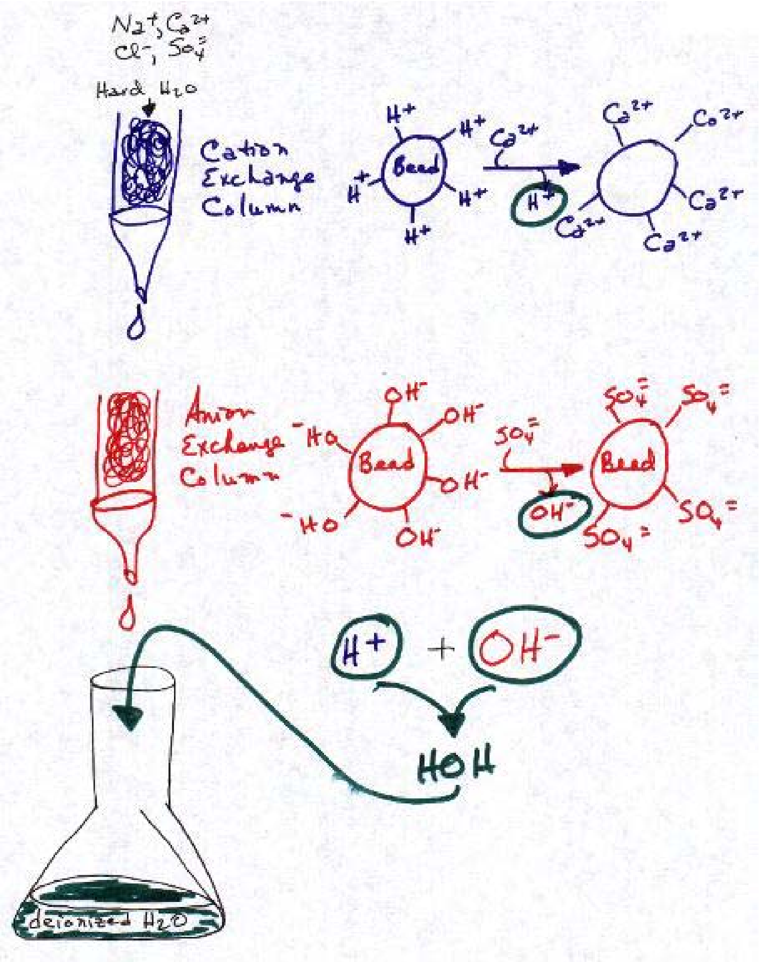




The $50 question is "how does one go about "softening" water, i.e., removing the calcium ions in this case from the water?" The figure at right illustrates the use of a cation and an anion-exchanging column.

The cation beads are soaked in acid so that protons bind to the beads. As the water is run through it, the cations in the water displace the protons and bind to the beads, themselves.

The beads in the anion exchanging column are soaked in base so that hydroxide ions bind to the beads. As the water runs through the anion exchanger, the anions in the water displace the hydroxide ions and bind to the beads, themselves.



After each ion is released from the beads, they combine to form water. This water is called de-ionized water and can be easily tested by electrical (conductivity) means for the level of purity -- remember a non-electrolyte solution will not conduct a current.

Uses of CO_2

CO_2 is not just a waste product -- it is a useful compound, as well. Dry ice (solid CO_2) is used to refrigerate ice cream, meat and frozen foods during shipment. One batch of dry ice is enough for one trip coast-to-coast. Liquid CO_2 (which exists ONLY under pressure) is used to inflate life rafts, make blasting shells for coal mining and as propellant in aerosol cans and fire extinguishers. Gaseous CO_2 is used to carbonate drinks.

Gaseous CO_2 is also used in the manufacture of urea:

$$CO_2(g) + 2NH_3(g) + 185^\circ\ C + 200\ atm \rightarrow CH_4N_2O\ (urea) + H_2O(l)$$

SO_2 (from fossil fuel use/burning) is removed from/by scrubbers in the stacks of power plants and furnaces as CO_2 is released:

$$Na_2CO_3(s) + SO_2(g) \rightarrow Na_2SO_3(g) + CO_2\uparrow$$

CO_2 is necessary for bread dough to rise:

$$NaHCO_3 + \text{Vinegar or Sour milk or salt hydrolysis} \rightarrow CO_2\uparrow + Na^+ + H_2O(l)$$

CO_2 fire extinguishers work via the following reaction:

$$2NaHCO_3(s) + 270^\circ\ C \text{ or greater} \rightarrow Na_2CO_3(s) + CO_2\uparrow + H_2O\uparrow$$

CO_2 is endothermic and cools the burning material. The density of CO_2 is greater than the density of air and the CO_2 forms a "blanket" over the fire, displacing the air and the fire goes out. BUT! Do NOT use CO_2 extinguishers with active metal fires:

$$CO_2(g) + Mg(s) + \text{fire} \rightarrow MgO(s) + CO\uparrow$$

The MgO keeps on burning, therefore, use powdered graphite extinguishers for these types of fires.

Cyanides

HCN = hydrogen cyanide or prussic acid. It is a colorless gas or liquid. It has the odor of bitter almonds. The average lethal dose is 50-60 mg and is produced as follows:

$$NaCN(aq) + H^+ \rightarrow HCN\uparrow + Na^+$$

The industrial production of HCN occurs by one of two methods and follows:

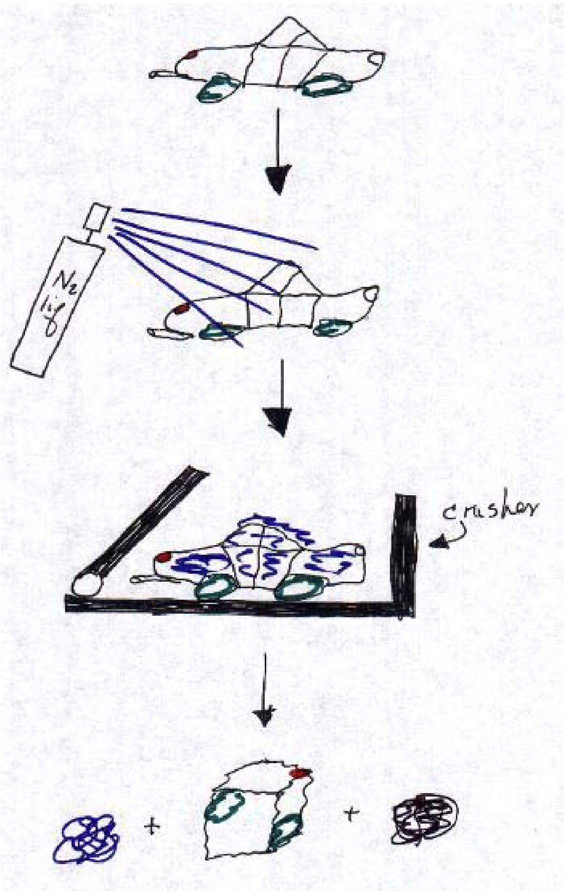
$$2CH_4(g) + 2NH_3(g) + 3O_2(g) + 1100° C + 2 \text{ atm} + \text{catalyst} \rightarrow 2HCN\uparrow + 6H_2O\uparrow$$

OR

$$CH_4(g) + NH_3(g) + 1250° C + \text{catalyst} \rightarrow HCN\uparrow + 3H_2\uparrow$$

60% of the US production of HCN is used to synthesize methyl methacrylate which is a monomer of Lucite and Plexiglass. 15% of HCN production is for NaCN synthesis. Cyanide is also used to extract gold and silver from their ores:

$$8NaCN(aq) + 4Au(s) + 2H_2O(l) + O_2(g) \rightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$$



The $Na[Au(CN)_2]$, above, is a complex salt of gold.

HCN is used to kill rats and mice in grain bins and ship holds. HCN is used in gas chambers in states with the death penalty by gas inhalation.

Nitrogen and Nitrogen Compounds

Mineral sources of nitrogen compounds include saltpeter (KNO_3; India) and Chilean saltpeter ($NaNO_3$).

Nitrogen's physical properties include being a colorless, odorless, tasteless gas that boils at -195.8° C at 1 atm; it freezes at -210° C.

N_2 is the most stable diatomic molecule known.

Chemical properties of nitrogen include being very stable. It reacts with Li, Ca and Mg to form nitrides (N_3^-); at moderate temperatures it reacts with hydrogen to form ammonia. The electronegativity of N_2 is exceeded ONLY by oxygen and fluorine. Another use of nitrogen is shown in the figure at right.

In this figure, nitrogen is sprayed on junk cars so that when they are crushed, it is easy to separate the steel (brittle like glass under these conditions) from copper and aluminum.

Nitrogen may be present in any one of 9 different oxidation states:

Oxidation State of the N	Formula	Name
-3	NH_3	Ammonia
-2	N_2H_4	Hydrazine
-1	NH_2OH	Hydroxylamine
0	N_2	Nitrogen
+1	N_2O	Nitrous oxide
+2	NO	Nitric oxide
+3	HNO_2	Nitrous acid
+4	NO_2	Nitrogen dioxide
+5	HNO_3	Nitric acid

Nitrogen is the 5th commonest element in the universe. KNO_3 and $NaNO_3$ occur ONLY in dry areas (remember that nitrates are water-soluble).

Free elemental nitrogen can be formed via decomposition reactions, e.g.,

$$NH_4NO_2 + \text{Heat} \rightarrow N_2\uparrow + 2H_20(l)$$

OR

$$2NaN_3 + 300^\circ\text{ C} \rightarrow 2Na(l) + 3N_2\uparrow$$

At room temperature, nitrogen reacts with lithium as follows:

$$6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$$

and with some metal complexes as follows:

$$[Ru(NH_3)_5(H_2O)]_2+(aq) + N_2(g) \rightarrow H_2O + [Ru(NH_3)_5(N_2)]^{2+}$$

and with nitrogen fixating bacteria.

Ammonia is the hydride of nitrogen. It is easily synthesized in the lab as follows:

$$NH_4Cl(s) + OH^-(aq) \rightarrow NH_3\uparrow + H_2O(l)$$

NH_3 is colorless, has a characteristic odor and is extremely soluble in water -- approximately 90 g of NH_3 dissolves per 100 mL of water at room temperature and 1 atm. Ammonium carbonate is smelling salts. Ammonium nitrate is used as a fertilizer. Under decomposition, though, ammonium nitrate reacts as follows:

$$2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O\uparrow + O_2\uparrow$$

The products occur during the explosive decomposition. 1 mol of solid ammonium nitrate will produce 3.5 mol of gas. This is characteristic of explosive reactions, i.e., a small amount of solid produces a large amount of gas.

Hydrazine (N_2H_4) is another hydride of nitrogen. It is synthesized as follows:

$$2NH_3(aq) + NaOCl + \text{glue or gelatin} + OH^- \rightarrow H_2NNH_2(aq) + NaCl(aq) + H_2O(l)$$

Hydrazine is stable at room temperature; it explodes during distillation if there is even a trace of air present. Hydrazine is used as rocket fuel and to remove oxygen from high pressure boiler water in power stations:

$$N_2H4\ (aq) + O_2(aq) \rightarrow N_2\uparrow + 2H_2O(l)$$

ASIDE: Remember the boiler explosions that occur as a result of scale formation?

$$3Fe + 4H_2O(g) + \text{heat} \rightarrow Fe_3O_4 + 4H_2\uparrow$$

$$4H_2(g) + \text{fire} \rightarrow \text{Explosion!!!!}$$

END of ASIDE

Nitric Acid and Nitrates

The manufacture of nitric acid is a multi-stepped series of reactions:

$$\text{First: } 4NH_3(g) + 5O_2(g) + Pt + 920°\ C + 7\ atm \rightarrow 4NO\uparrow + 6H_2O\uparrow$$

$$\text{Second: } 2NO(g) + O_2(g) \rightarrow 2NO_2\uparrow$$

$$\text{Third: } 3\ NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO\uparrow$$

REMEMBER: NO_2 and NO are NOT the acidic anhydrides of nitric acid:

Compound	NO_2	NO	HNO_3
Oxidation state of N	+4	+2	+5

The acidic anhydride of nitric acid is N_2O_5:

$$N_2O_5 +(s) + H_2O(l) \rightarrow 2HNO_3(aq)$$

The N in both reactant and product is in the +5 state, i.e., no oxidation state change!

In the lab, nitric acid is produced as follows:

$$NaNO_3(s) + H_2SO_4(l) + \text{distillation} + \text{reduced pressure} + 0^\circ\ C \rightarrow HNO_3(l) + NaHSO_4(s)$$

Pure nitric acid is colorless. Once light reacts with it, it turns yellow due to increased NO_2 formation in solution. Nitric acid's number one use is for fertilizers. Second highest use is for explosives. Other uses include use in the steel industry, in dye manufacture, in plastics and in synthetic fibers.

Nitric acid reacts with metals that do NOT react with non-oxidizing acids like HCl and phosphoric acid. Hot concentrated nitric acid dissolves nearly ALL metals except Au, Pt, Ir and Rh. Listed below are representative reactions involving nitric acid:

$$Cu(s) + 4HNO_3\ (16M) \rightarrow Cu(NO_3)_2(l) + 2NO_2\uparrow + 2H_2O(l)$$

$$3Cu(s) + 8HNO_3\ (6M) \rightarrow 3Cu(NO_3)_2(l) + 2NO\uparrow + 4H_2O(l)$$

$$C(s) + 4HNO_3\ (16M) \rightarrow CO_2 + 4NO_2\uparrow + 2H_2O(l)$$

$$3Zn(s) + 8HNO_3\ (6M) \rightarrow 3Zn(NO_3)_2(aq) + 2NO\uparrow + 4\ H_2O(l)$$

$$4Zn(s) + 10\ HNO_3\ (3M) \rightarrow 4Zn(NO_3)_2(aq) + N_2O\uparrow + 5H_2O(l)$$

$$5Zn(s) + 12\ HNO_3\ (1M) \rightarrow 5Zn(NO_3)_2(aq) + N_2\uparrow + 6H_2O(l)$$

$$4Zn(s) + 10HNO_3\ (0.1M) \rightarrow 4Zn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

("N's" in **blue**, above, are in the +5 state; in **red** in the +4 state; in **green** in the +2 state; in **fuschia** in the +1 state; in **black** in the -3 state and in **brown** in the zero (elemental) state.)

In general, the greater the concentration of the acid, the less the oxidation state change. This is easily explained, below:

Concentrated acid has LOTS of nitrate to be reduced, therefore each nitrate is only able to obtain a very few electrons.	Dilute acid has very few nitrates to be reduced, therefore each nitrate is able to obtain a LOT of electrons.

Nitric acid oxidizes compounds as well as elements:

$$3CuS(s) + 8HNO_3\ (3M) + \text{heat} \rightarrow 3Cu(NO_3)_2(aq) + 3S(s) + 2NO\uparrow + 4H_2O(l)$$

NO is colorless; CuS is very insoluble.

The xanthoproteic reaction occurs between nitric acid and proteins (look at your skin when you spill nitric acid on it) and turns yellow.

Nitrous Acid and Sodium Nitrite

HNO_2 is a weak acid. It can not be isolated as it's a multi-stepped reaction or when it's warm.

$$3HNO_2\ (aq) \rightarrow HNO_3(aq) + 2NO\uparrow + H_2O(l)$$

Nitrous acid is prepared as and when needed:

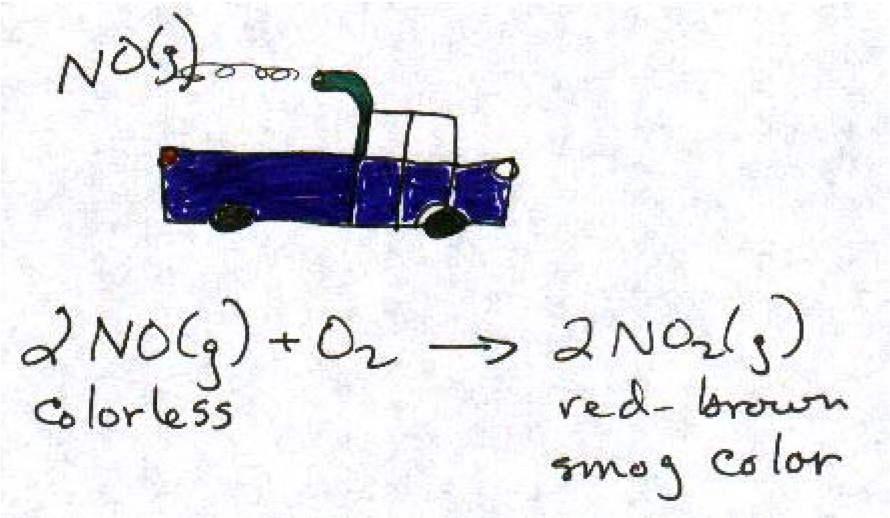
$$HCl(aq) + NaNO_2(aq) + 0°\ C \rightarrow HNO_2(aq) + NaCl(aq)$$

It must be used immediately.

Sodium nitrIte is prepared by heating sodium nitrAte to decomposition with the loss of molecular oxygen.

Smog

The figure at right illustrates one way in which cars contribute to smog. In general, the combustion of gasoline with air in the presence of the catalytic converter causes the formation of NO. The colorless NO reacts with oxygen to form red-brown NO_2 which gives smog its



brownish color. The "treatment" for this has been to add oxy-fuel additives. The most commonly used additive was MTBE. Of course, we are aware of the politics surrounding MTBE in this neck of the woods.

Uses of Nitrogen Compounds	
Fertilizer	Ammonia
Hydrazine	Rocket fuel
Azides	NaN_3 = antibiotic; $Pb(N_3)_2$ = detonator for military explosives
Acids	Nitric and nitrous acids; aqua regia (3 parts HCl and 1 part nitric acid)
Nitroglycerine	Used in dynamite production and as vasodilator
Gun cotton	Cotton nitrated in the presence of sulfuric acid, aka nitrocellulose
TNT	2,4,6-trinitrotoluene
Black powder	KNO_3, C, S
Ammonal	Ammonium nitrate and aluminum powder -- explosive
Nitrates	Fertilizers
Anesthetic	N_2O = laughing gas

Nitrogen-containing Organic Compounds	
Urea	#1 fertilizer; has the greatest amount of nitrogen (47%)
Acrylonitrile	Monomer of Acrilan, Creslon and Orlon
Caprolactam	Used to make nylon-6 (ropes and tire cord)
Hexamethylene diamine	Used to make nylon-66 (first nylon made)

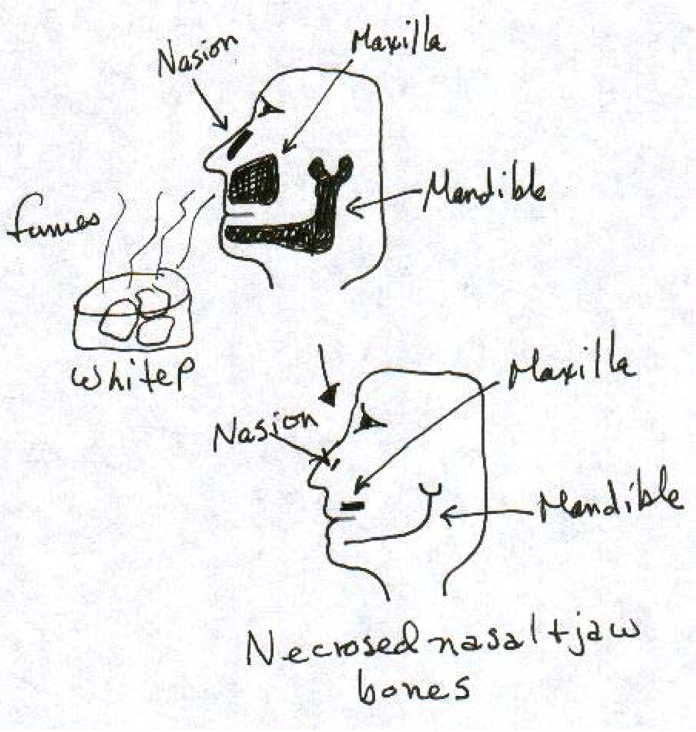
Phosphorus and Its Compounds

P is more metallic than nitrogen. The electronegativity (EN) of P is 2.1; that of N is 3.0.

Phosphorus is active at low temperatures. White phosphorus is unstable; red P is stable.

PH_3 (hydride of phosphorus called phosphine) is a stronger reducing agent than ammonia. Bones, teeth, muscle, nerves contain phosphorus.

The primary commercial source of phosphorus is phosphate rock, which contains lots of calcium phosphate with other phosphates, as well.

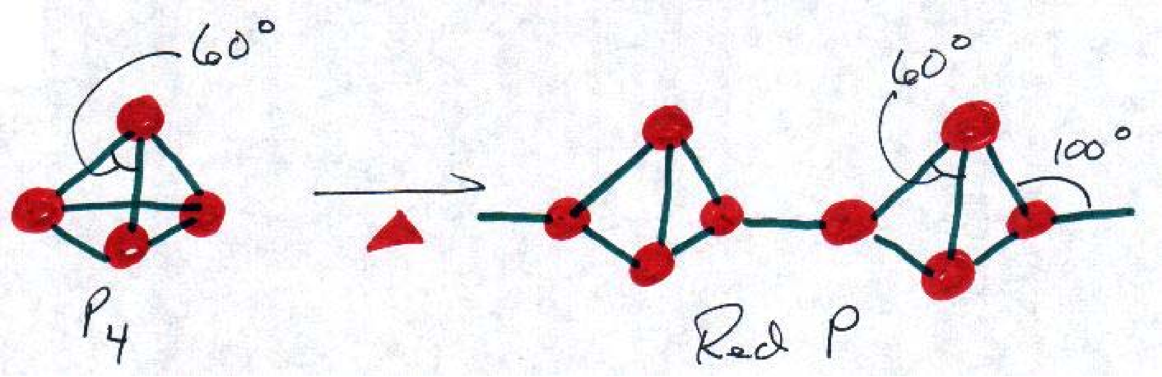


150 mg of white phosphorus can cause acute pain, convulsions and, possibly, death. When the fumes of white phosphorus are continuously breathed in, right, they cause necrosis of the nasal and jawbones (maxilla and mandible). In very small doses, phosphorus stimulates the nervous system.

In terms of the physical properties of P, it is available as white or red P. When white P reacts with light, it forms "yellow P"; "yellow" P is white P with a light coating of red P on its surface.

White P is very soluble in CS_2; not soluble in ether or chloroform and is very nearly insoluble in water. White P exists as P_4.

The exact structure of red P is not definitely known, but it resembles a fractured tetrahedron, below:



Chemical Properties: the most important chemical property of P is its chemical activity towards molecular oxygen. When White P is stored at room temperature, it undergoes a slow oxidation. During this process, its temperature rises. When the temp hits between

35 and 45° C, it spontaneously ignites. Storing White P under water stops all of these oxidative processes and does not allow spontaneous combustion to occur. Burns from white P are painful and slow to heal, which is why "WP" (white P) mortar rounds were used in various wars. Handle WP only with forceps and put in water immediately after use.

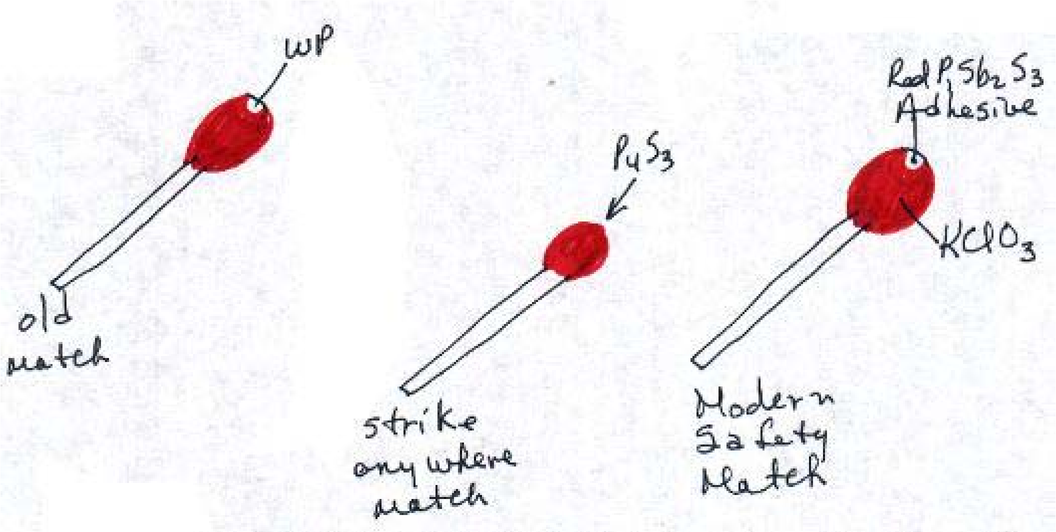
Moist WP also may undergo slow oxidation in air to form phosphoric acid, phosphorous acid, phosphorescence and ozone. When P is heated in the presence of oxygen, P_4O_{10} forms. The P_4O_{10} reacts with moist air to form a fog of minute phosphoric acid droplets.

Red P does not ignite until about 250° C. The products are still the same as with the WP.

Uses of Phosphorus

From 1831 to the end of the 19th century, WP used to be in matches,below. Since WP is poisonous and causes osteonecrosis, WP was replaced by P_4S_3 to make "strike anywhere" matches. Modern safety matches contain red P, Sb_2S_3 and an adhesive in their tips and $KClO_3$ as the oxidizer below the tip. When the match is truck, friction heats $KClO_3$ causing red P and Sb_2S_3 to catch fire that burns the cardboard or wood (fuel).

Phosphorus-containing compounds are used as fertilizers, baking powders, alloys, fireworks, bombs, rat poisons, smoke screens and smoke grenades.



The most important inorganic compound of P is phosphoric acid (H_3PO_4). It is synthesized as follows in the 2 reactions below:

$$P_4(l) + 5O_2(g) + \text{heat} \rightarrow P_4O_{10}(s)$$

$$P_4O_{10}(s) + 6H_2O(g) \rightarrow 4H_3PO_4$$

P_4O_{10} is called phosphorous pentoxide after its EMPIRICAL formula: P_2O_5; it is the P_2O_5 which is the acid anhydride of phosphoric acid. 0.05% phosphoric acid is added to Coca Cola (Coke) to make it taste tart at a pH of about 2.3.

Phosphoric acid auto-ionizes:

$$2H_3PO_4(l) \Leftrightarrow H_4PO_4^+ + H_2PO4^-$$

This, then, is an electrolyte.

The figure below takes you through the dissociation of phosphoric acid and through the dissociation constants for each dissociative step to, eventually, obtain the overall acid dissociation constant. Since phosphoric acid is triprotic, 3 kinds of salts may be synthesized:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$

$$H_2PO_4^- \rightleftharpoons HPO_4^= + H^+$$

$$HPO_4^= \rightleftharpoons PO_4^{\equiv} + H^+$$

$$K_1 = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} \qquad K_2 = \frac{[HPO_4^=][H^+]}{[H_2PO_4^-]}$$

$$K_3 = \frac{[PO_4^{\equiv}][H^+]}{[HPO_4^=]}$$

$$K_{overall} = K_1 \cdot K_2 \cdot K_3$$

$$K_{overall} = \frac{\cancel{[H_2PO_4^-]}[H^+]\cancel{[HPO_4^=]}[H^+][PO_4^{\equiv}][H^+]}{[H_3PO_4] \quad \cancel{[H_2PO_4^-]} \quad \cancel{[HPO_4^=]}}$$

$$= \frac{[H^+]^3[PO_4^{\equiv}]}{[H_3PO_4]} = K_{overall}$$

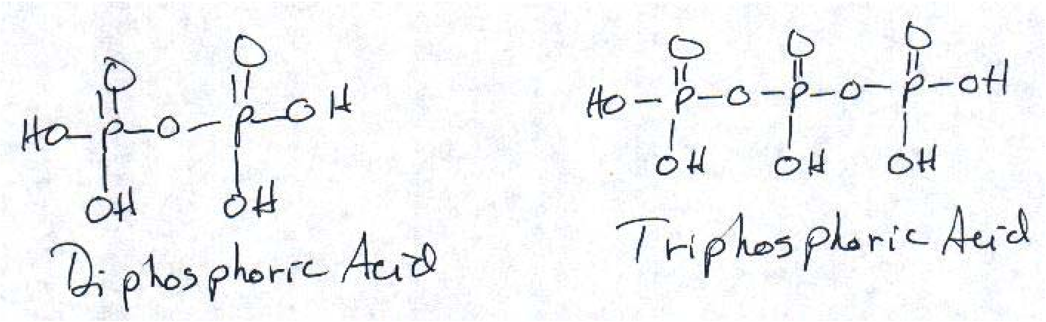
First dissociation	Second dissociation	Third dissociation
H_3PO_4 (XS; aq) + $Na_2CO_3(aq) \rightarrow 2NaH_2PO_4(aq) + CO_2\uparrow + H_2O(l)$	$H_3PO_4(aq) + Na_2CO_3$(XS; aq) $\rightarrow Na_2HPO_4(aq) + CO_2\uparrow + H_2O(l)$	$H_3PO_4(aq) + 3NaOH$(XS; aq) $\rightarrow Na_3PO_4(aq) + 3H_2O(l)$
		NaOH is used here as Na_2CO_3 is not strong enough to strip off the 3d proton
Salts formed, respectively		
NaH_2PO_4 is water soluble. It is used to adjust the pH of water for boilers and in laxative tablets that fizz (with $NaHCO_3$): NaH_2PO_4 (aq) + $NaHCO_3(aq) \rightarrow CO_2\uparrow + Na_2HPO_4(aq) + H_2O(l)$	Na_2HPO_4 is used in pudding mixes and quick-cooking cereals. It is basic.	Na_3PO_4 is very basic. Used in scouring powders and paint removers.
Useful Calcium salts		
$Ca(H_2PO_4)_2\cdot H_2O$ -- used in baking powders	$CaHPO_4\cdot 2H_2O$ -- in toothpaste	$Ca_2P_2O_7$ (calcium diphosphate) is insoluble, inert, abrasive -- used in toothpaste with SnF_2 (Stannous fluoride)

Disodium hydrogen phosphate reacts with sodium dihydrogen phosphate as follows to form sodium triphosphate, aka sodium tripolyphosphate:

$$2Na_2HPO_4(s) + NaH_2PO_4(s) + 450^\circ\ C \rightarrow Na_5P_3O_{10}(s) + 2H_2O\uparrow$$

Sodium tripolyphosphate used to be used as the "builder" for synthetic detergents. Hard water, remember, contains calcium and magnesium divalent cations. These cations form complexes with triphosphate. High levels of these complexes, when dumped into bodies of water, cause eutrophication. This is brought about due to the high levels of phosphorous. These high levels increase algal growth. As the algae multiply and grow, they begin to decay and take up large amounts of oxygen from the water. This loss of oxygen kills the fish in the water. Laws were enacted prohibiting the use of tripolyphosphate as detergent builders, so industry used sodium carbonate as the builder. Calcium and magnesium carbonates are formed which softens the water and cleans the clothes.

There are two other acids of phosphorus: Diphosphoric (or pyrophosphoric) acid and triphosphoric acid:



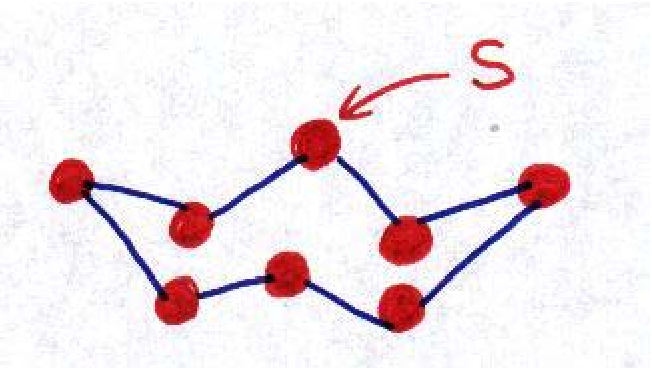
Properties of the Sulfur Family

The table, below, summarizes some of the chemical and physical properties of the members in this family:

Element	O	S	Se	Te
Physical state	Gas	Solid	Solid	Solid
Color	Colorless	Yellow	Red or grey	Silver
Electronegativity	3.5	2.5	2.4	2.1
Oxidation states	-1, -2	-1, -1, +1, +2, +3, +4, +6, +7	-2, +1, +4, +6	-2, +4, +6
Ionic radius of divalent anion (Å)	1.4	1.84	1.98	2.21

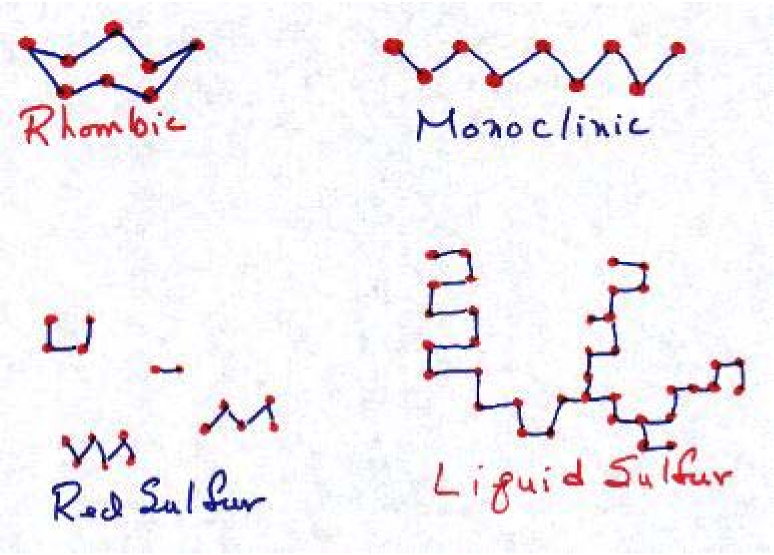
Sulfur

The S-S bond is the 3d strongest bond. Only the H-H and C-C bonds are stronger. At room temperature, sulfur exists in the form of rhombic sulfur. Note the shape of this form of sulfur: an S_8 ring that is crown-shaped, right:



The structure of sulfur-forms gets very complex very quickly. The figure, below, illustrates 4 different forms of sulfur. These graphics correspond with the text, following.

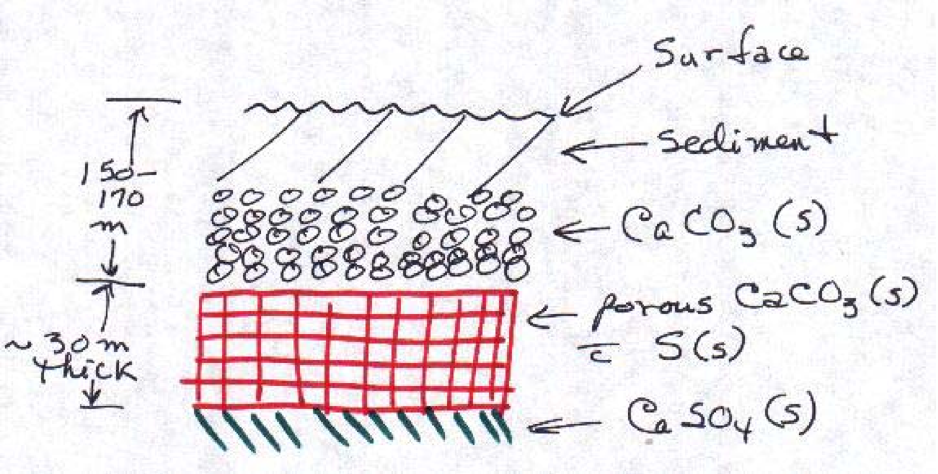
Rhombic sulfur is yellow powder or crystals. When heated from room temperature to 96° C, the ring ("crown") breaks to form yellow monoclinic sulfur. When monoclinic sulfur is heated up to between 160-195° C, it polymerizes, forming a polymer that consists of more than 200,000 sulfur atoms. This form of sulfur is called liquid sulfur, is orange in color and has a viscosity that is 100,000 fold greater than monoclinic sulfur due to ring opening and polymer formation. With the temperature going above 195° C, liquid sulfur depolymerizes to give red sulfur with a greatly reduced viscosity due to shorter chains.



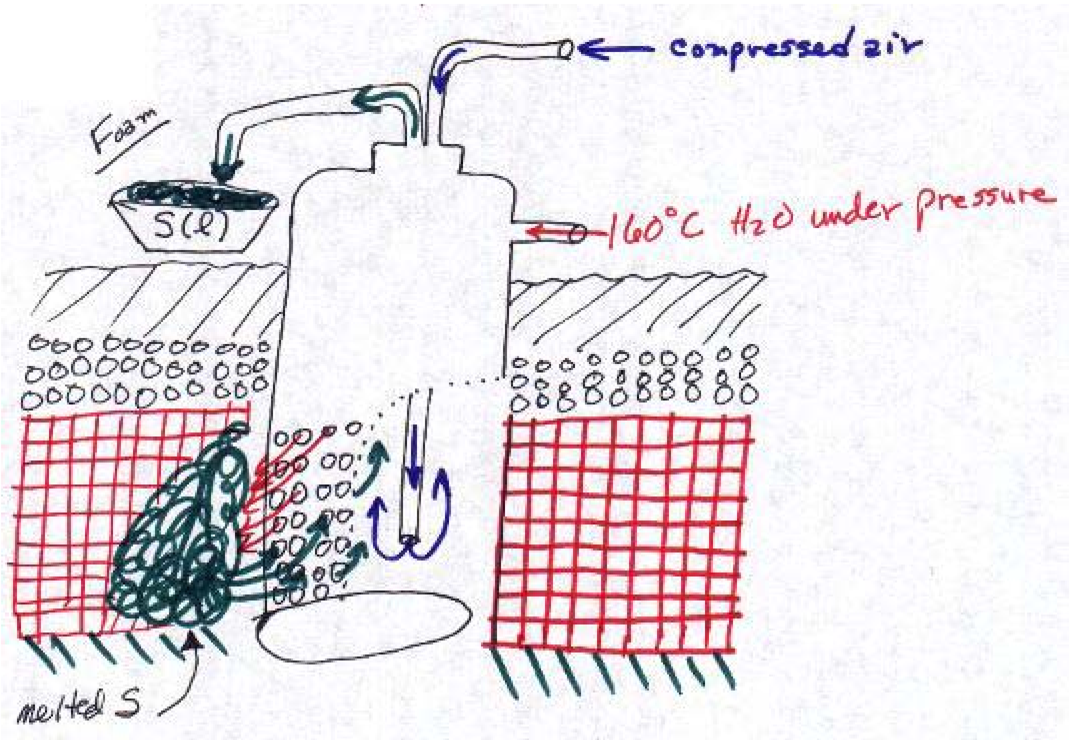
If one pours liquid sulfur into cold water, amorphous, "plastic" sulfur (threads of sulfur) forms in coiled chains. If these coils are stretched, they stretch just like a spring. Gradually, amorphous sulfur closes the chains into crowns to [re]form rhombic sulfur.

Sulfur reacts with all elements except: nitrogen, Te, iodine, Ir, Pt, Au and anything in Group VIII.

The figure, following, illustrates a cutaway across the earth. This cutaway illustrates where stores of



sulfur are found beneath the earth. Note that the layer of calcium sulfate is the ultimate source of sulfur. Calcium sulfate is reduced by bacteria to form elemental sulfur. The commercial production of sulfur is accomplished by the Frasch process. In short, one drills a hole with regular oil-well equipment and inserts 3 concentric pipes:



The way this process works is to shoot hot compressed air -- not too fast as the sulfur will precipitate if it's too fast -- down one of the concentric tubes. At the same time, water at 160° C under pressure is shot into the porous calcium carbonate layer where the sulfur is. The hot water melts the sulfur. Since the density of the sulfur is greater than the density of water, the sulfur settles to the bottom of the deposit and then is forced out by the hot compressed air. The sulfur, then, is obtained as a foam. To "bleed off" excess amounts of water so that pressure doesn't build up, wells are drilled below the sulfur "well" to collect the water. Sulfur is transported primarily in the liquid form in the US.

In the lab, sulfur is obtained in a two-step process:

$$2H_2S(g) + 2O_2\,(g;\ \text{limited}) + 400^\circ\ C \rightarrow S(l) + SO_2\uparrow + 2H_2O$$

The gaseous SO_2 is then reacted as follows:

$$SO_2(g) + 2H_2S\ (g;\ XS) + Fe_2O_3 + 300^\circ\ C \rightarrow 3S(l) + 2H_2O\uparrow$$

Sulfuric Acid and Sulfates

$$4FeS_2(s) + 11\ O_2(g) + \text{roasting} \rightarrow 8SO_2\uparrow + 2Fe_2O_3{}^{-}$$

The gaseous SO_2 produced is used for the production of sulfuric acid. This is a three step process:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3\uparrow$$

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l) \leftarrow \text{Disulfuric acid}$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

Sulfuric acid is the cheapest strong acid manufactured. Sulfuric acid is a diprotic acid. The dissociation of the first proton is 100% complete in dilute solution and is, **probably**, between a pK_a of 0 and 1. The dissociation of the second proton has a K_a of $1.2*10^{-2}$, i.e., a pK_a of about 1.92. This is very acidic. On a biological note, the chemistry just ain't there to support making sulfuric acid in any part of the human body as the pH in the body just doesn't get low enough to defeat the first K_a.

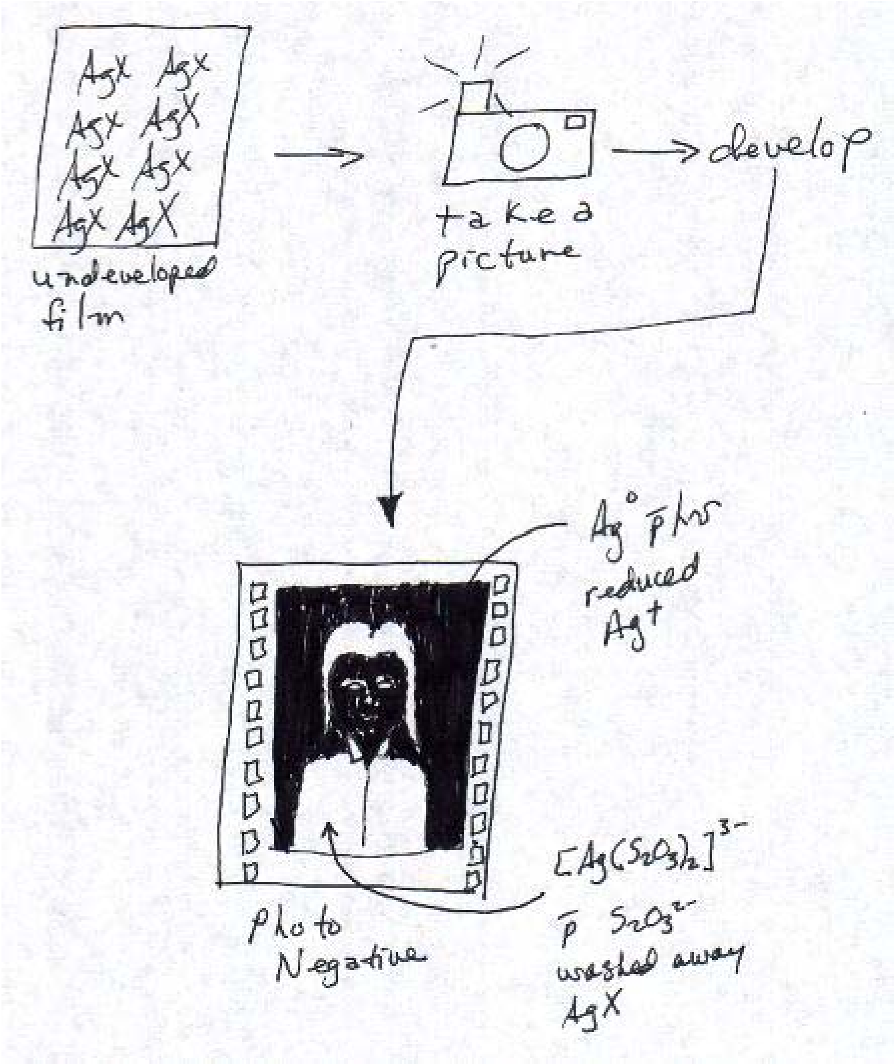
Sulfuric acid will react with metals like elemental copper to form copper (II) sulfate, water and sulfur dioxide gas when heated.

Three sulfates are in the "Top 50" chemicals sold in the US and are tabulated, below:

$Al_2O_3 \cdot 2H_2O(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 5H_2O(l)$	$2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl$	$H_2SO_4(aq) + 2NH_3(g) \rightarrow (NH_4)_2SO_4(aq)$
The first reactant on the left is bauxite; the first product is used as a water clarifier and to fill pores in paper.	The first product is used in the manufacture of brown paper bags and brown wrapping paper.	The product of this reaction is used as fertilizer.

An important oxo-acid of sulfur is thiosulfuric acid, $H_2S_2O_3$. It is important in the production of a salt, $Na_2S_2O_3$, sodium thiosulfate. The significance of this salt is as illustrated in the reaction, below:

$$AgX(s) + 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + X^-, \text{ where "X" = a halogen}$$



This is important in photography, right. Undeveloped film is impregnated with AgX. Take the picture and send it in for developing and that's it, right? Nope! AgX dissociates to Ag^+ and X^-. When regions of the film that have ionized Ag on it are "hit" by light, the Ag^+ is reduced to Ag^0. The regions of the film with Ag^0 on it are the dark parts of the negative; conversely, the Ag^+ that is not reduced reacts with the $S_2O_3^{2-}$ to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$. When the complex ion is washed away, it makes the clear area of the negative. The other name for the $S_2O_3^{2-}$ is "hypo".

Sulfur Oxides

Of primary importance are two oxides: SO_2 and SO_3. These are the most stable oxides. SO_2 is a colorless gas that has a sharp odor. It the most dangerous pollutant. It comes from burning fossil fuels that are burned in power plants, homes, cars, roasting sulfide ores, volcanoes and marsh gases due to air oxidation. SO_2 is used as a bleach and as an antibacterial to preserve fruit.

As mentioned above, SO_2 is the most dangerous pollutant. This is because SO_2 reacts with dust and water in polluted air to form SO_3. SO_3 is generally a liquid and the acid anhydride of sulfuric acid. It's also hard to handle as it's so reactive. SO_3 in the air mixes with NO_2 and HCl and water to form acid rain. Acid rain is responsible for killing forests and for, literally, dissolving limestone and marble buildings and statues.

Sulfides

In qualitative analysis, H_2S is generated from a compound called thioacetamide (TA), the thioamide of acetic acid (C_2H_5NS). When TA is hydrolyzed with the addition of water and heated, the only stable "hydride" of sulfur is formed: H_2S. This smells like rotten eggs and is about 200 times as poisonous as cyanide. It is so much more poisonous because it anesthetizes the sense of smell (cranial nerve I), so people keep breathing it in and they die -- no, not enough H_2S is generated in lab, here, to cause death.

One very common reaction of silver with sulfur is:

$$4Ag(s) + 2H_2S(g) + O_2(g) \rightarrow 2Ag_2S(s) + 2H_2O(l)$$

The Ag_2S is greenish/black and is the tarnish on Grandma's good silver that has to be polished regularly.

Experimental

Detection of Nitr**a**te Ions

The detection of nitrate using an alkaline solution of sodium nitrate mixed with Devarda's Alloy to produce ammonia was performed as an introductory qual test in Chapter 1. The method used in this experiment is called the "Brown Ring Test".

Place about a half a pea-size amount of sodium nitrate in a disposable test tube with a spatula. Dissolve it in a minimal amount of distilled water. In another test tube, mix 0.1 g ferrous sulfate heptahydrate in 1 mL of distilled water. Mix the contents of the two tubes together.

CAREFULLY slant the test tube of the 2 solutions away from your face and CAREFULLY decant concentrated sulfuric acid down the side of the tube from a disposable pipet to make a layer in the bottom of the tube about 1 cm in height. Set the test tube in the rack and leave undisturbed for at least 5 minutes. The presence of a brown ring at the interface between the layers is conclusive for nitrate ion. The brown ring is due to the formation of the complex nitrosyliron(II) ion ($Fe(NO)^{2+}$).

Detection of Nitr**i**te Ions

Nitrite ions give the same complex ion when tested as the nitrate ions – only moreso – the brown/green color is throughout the whole solution.

Add about a quarter sized sample of sodium nitrite to a test tube and dissolve it in a minimum of distilled water. In another test tube, mix 0.1 g ferrous sulfate heptahydrate in 1 mL of distilled water. Mix the contents of the two tubes together.

CAREFULLY slant the test tube of the 2 solutions away from your face and CAREFULLY decant concentrated sulfuric acid down the side of the tube from a disposable pipet to make a layer in the bottom of the tube about 1 cm in height. Set the test tube in the rack and leave undisturbed for at least 5 minutes. The presence of a brown/green solution (OR ring) at the interface between the layers is conclusive for nitrate ion. The brown ring is due to the formation of the complex nitrosyliron(II) ion ($Fe(NO)^{2+}$).

Detection of Sulfide Ions

This test is best performed in the hood. Place a few flakes of sodium sulfide in a well in your spot plate. Add 2 drops of 4 or 6 or 8M sulfuric acid on top of the flakes. CAUTIOUSLY waft the vapors to your nose and see if you can identify the rotten egg odor. That odor is positive for the presence of sulfide ion.

Another way to test for sulfide ion is to repeat the above experiment without wafting the vapors – instead, hold a moistened piece of lead acetate paper by forceps or a clothes-pin over the sample. A brownish black or silvery black coloration (lead sulfide) of the paper is positive for sulfide.

Detection of Sulfate Ions

In a clean disposable test tube, place about a quarter the size of a pea's worth of sodium sulfate and dissolve it in a minimum of distilled water. Add an equal volume (no more than 1 mL) of 6M hydrochloric acid to the solution and mix. To this new solution, add a few drops of 1M barium chloride and observe for a fine white precipitate. This white precipitate (barium sulfate) may be difficult to see, yet is positive for the presence of sulfate ions.

Detection of Phosphate Ions

Place about a quarter of the size of a pea's worth of trisodium phosphate dodecahydrate in the bottom of a clean disposable test tube and dissolve it in a minimum of distilled water. To the solution, add just enough 6M nitric acid to make the solution acidic to litmus. At this point, add 0.5 mL magnesia mixture and set the tube aside after mixing. A slow-forming (usually) white precipitate (magnesium ammonium phosphate – a.k.a. triple phosphate) is positive for the presence of phosphate ions.

Detection of Carbonate Ions

Place about a quarter the size of a pea's worth of sodium carbonate in a clean dry disposable test tube with a spatula. Dissolve it in a minimum of distilled water. Add concentrated ammonia a drop at a time with stirring until the solution is just alkaline. At this point, add several drops of 0.2 M barium chloride solution. A white precipitate of barium carbonate is positive for carbonate.

Reagent Disposal

When you have completed your experiments, pour the contents of all of your disposable test tubes into the container your professor has provided. Rinse the tubes and dispose of them in the broken glass container. Clean up your lab bench area and wash your hands before you leave. Remember: if you have extra time at the end of the lab period, that's the perfect time to ask for help with any questions you have in the course. Complete the problem set that follows for check off at the beginning of the next lab period.

Problem Set -- Anions and General

1. Using the periodic table, below, color the "squares" that have the non-metal in anions with a colored pencil. You will use this table again, so prepare it carefully.

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

2. Write the reaction that occurs when S^{2-} reacts with lead acetate (PbOAc) paper.

3. Which of the following are proton donors? proton acceptors? Write the reactions for the following pairs of compounds:

A. Nitric acid and magnesium hydroxide
B. Acetic acid and sodium carbonate
C. Zinc and hydrochloric acid
D. Carbon dioxide and potassium hydroxide

4. Given the following reaction:

$$3HNO_2 + Fe(OH)_3(s) \rightarrow Fe^{3+} + 3NO_2^- + 3H_2O$$

derive the expression for the K_{eq} and demonstrate that the K_{eq} is some combination of $K_a(HNO_2)$, K_w and $K_{sp}(Fe(OH)_3)$ (all found in the CRC). Based on your value for the K_{eq}, would you expect this reaction to "go"? Why or why not?

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