**Chromium Revisited**

A stroll through the oxidation states and colors of Chromium. Pt1.

About 25 yrs. ago I did a series of simple experiments to show my teenaged son how varied this fascinating element’s chemistry was. Recently I felt a yen to repeat these and did so. I thought it might be worth while to suggest some ideas, and chromium seems to be rarely mentioned, so here goes.

Note 1: *All chromium compounds are poisonous, in the order Cr[II] < Cr[III] << CrO4 - - and Cr2O7- - . Figures for LD50 rat oral are approx. 1900,1800,180, 25 mg/kg. NACN is around 6mg/kg. Hence the chromates are very poisonous, about 1/4 as lethal as cyanide. They can be absorbed though the skin, so wear gloves.*

Note 2: The colors quoted here are as I perceive them, in daylight under partly cloudy skies. In general many of the Cr compounds show quite different colors in artificial light, different grades of fluorescent and especially incandescent, due to illuminating spectrum. Eyes differ – my wife sees blues where I see greens. Photo sensors also vary – the only way is to see them for yourself and decide. Do the experiments!

I will run through the oxidation states of Cr, starting at 0, the metal itself (and, due to the definition used, that of a few organic Cr compounds such as carbonyl, Cr(CO)6).

(1) **Metallic Cr, Cr[0],** can be made by the amateur quite easily by thermite reduction of the oxide Cr2O3 (lots of data on this site, UTSE). Another method is by electrolysis of acidified Cr2(SO4)3 on to a copper cathode. Good hard shiny coatings are hard to do and usually the coat can be peeled off. A mercury cathode can be used to make an amalgam. An iron cathode can be used (if inserted with current on) and will produce a black powered Cr metal easily scraped off.

The **Cr[I] oxidation** state does not exist as far as I know (AFAIK), nor do distinct hydrides, although the metal can occlude hydrogen like all transition metals.

(2) For the following experiments, prepare a saturated solution of about 50-100cc of a chromic Cr[III] salt, usually sulphate or chloride. Chrome Alum for growing crystals is often available and this is what I use, KCr(SO4)2.12H2O. This and the sulphate are both dark reddish-violet crystals. **DO NOT HEAT** to assist solution for reasons below, dissolve at RT, first grinding the alum or sulphate to a fine powder. {If you use the chloride, CrCl3.6H2O it will probably come as dark green crystals rather than violet}. In solution the alum acts the same as the sulphate, the K+ are merely spectator ions.

 (3) **Aqua Complexes:**

(3a) Heat a small amount of the violet (purple by transmitted light) solution of Cr[III] sulphate to boiling for a few minutes. The solution turns from violet to deep green. On cooling it preserves the green color. It will stay green for several days to weeks but finally return to the original violet. The green form is *chemically different* from the violet form as can be shown by precipitation of the sulphate ion with a barium salt, and also by electric conductivity or freezing point measurement. The green salt does not form a precipitate. The mystery was solved in the early 1900s; the violet ion is the complex Cr(H2O)6+++; the dark green one maybe [Cr(H2O)4(SO4)]+; or perhaps [Cr2(H2O)l0(SO4)]++++ or the covalent [Cr2(H2O)6(SO4)3], or a mixture of all three.

Only the violet form will crystallize. If the green form is heated to dryness, only green scales result. Further cautious heating produces an orange-yellow product which is the anhydrous form with perhaps some decomposition. Strong heating (bright red heat) causes decomposition and SO3 evolution: Cr2(SO4)3 🡪 Cr2O3 + 3SO3

 For the chloride of Cr[iii], Wiki has:

“**Chromium(III) chloride** (also called **chromic chloride**) is a violet coloured solid with the formula CrCl3. The most common form of CrCl3 sold commercially is a dark green hexahydrate with the formula [CrCl2(H2O)4]Cl.2H2O. Two other hydrates are known, pale green [CrCl(H2O)5]Cl2.H2O and violet [Cr(H2O)6]Cl3. This unusual feature of chromium(III) chlorides, having a series of [CrCl3−*n*(H2O)*n*]*z*+, each of which is isolable, is also found with other chromium(III) compounds.”

This indicates the facility with which Cr forms complexes, in this case with water. It is also interesting to note that both Cr[III] sulphate and chloride, if anhydrous, are virtually insoluble in water. The crystalline form of sulphate is Cr2(SO4)3.12H2O or, according to the above, [Cr(H2O)6]2(SO4)3.6H2O, and is very soluble.

(4) **Cr[III] Compounds**

{The temptation to insert a Pourbaix or Eo/pH diagram here was great – if you understand them they tell a lot at a glance. But many do not and it might merely confuse.}

The salts of Cr+++ with strong acids all give an acid reaction in solution – in other words Cr(OH)3 is a weak base; being a bit more technical, the ion Cr+++ has a pKa of about 4 whereas a strong base ion like Na+ has pKa~14.

(4a) Take a test-tube of the *violet sulphate* solution and drip in some fairly concentrated solution of NaOH (or KOH). Until the hydroxide neutralizes some of the acidity nothing happens, then a flocculent precipitate of a light gray-green color settles out. If too much hydroxide is added, this precipitate re-dissolves. The precipitate is hydrated Cr[III] hydroxide, Cr(OH)3.xH2O. If instead the green form of sulphate is used, the formation is slower but the same precipitate obtained. If done carefully, the liquid becomes colorless and depleted of Cr[III] ions. If the precipitate is left long enough (or centrifuged) the color becomes a very distinct green color and compacts, probably due to loss of water.

Reaction is simply Cr+++ + 3(OH)- + xH2O 🡪 Cr(OH)3. xH2O (s); x is approx. 3 when dried carefully. In alkaline solutions Cr[III] always exists as the hydroxide, except when the pH is high.

(4b)Addition of excess hydroxide causes the precipitate to redissolve giving a light green solution. This is usually stated to be due to chromite ion Cr(O2)-, or a hydrated form of this. This is still a Cr[III] ion, probably O=Cr—O-. Reducing the pH with acid re-precipitates the hydroxide.

(4c) Using NH4OH a similar precipitate with a grayish color is first formed. As further hydroxide is added carefully, again the liquid will clear. If excess ammonia is added, and the solution left for an hour or so, this gelatinous ppt. will turn a light purple, quite different in color from the sodium hydroxide case. On standing for a few days, or on prolonged boiling, the purple color disappears as ammonia is lost, leaving a gray-blue hydroxide. My guess is that the purple is a pentamminechromium complex; [Cr(NH3)5.(OH)x](3-x)(OH). yH2O.

{The colors of the Cr[III] ammine chloride complexes are; tri+++, yellow; tetraCl2+, green; pentaCl++, purple; non ionic tri Cr(NH3)3Cl3, violet and the ion Cr(NH3)2Cl4-, orange-red (Pauling, General Chem.)}.

See Brauer, p1345ff, for more on hydroxides and the organic complexes of Cr[III].

(4d) The **hydroxide** has a very low solubility product in water, about 6x10^-31. It can be purified by washing with large amounts of water and can be dried as a dull green powder, hydrated, and is a useful source of Cr[III] salts with common mineral acids. On heating to red heat it loses water to become a bright green oxide, 2Cr(OH)3 - -> Cr2O3 + 3 H2O. This oxide, the most stable form of Cr[III] under mild conditions, is usually insoluble in acids but can be reacted with *fused* alkali hydroxides to form chromates – see later on. Structure is O=Cr-O-Cr=O.

Most of the Cr[III] salts exist as blue-violet or green types when hydrated. As large crystals the violet forms look black; as powder, reddish. Chromium and potassium sulphate are isomorphous and crystallize together in all proportions, giving crystals that vary from lightest pink to almost black. Chrome alum is the equimolecular mixture. It can form massive octahedral crystals with patience – I have grown them up to 7cms. long looking as black as coal.

Insoluble Cr[III] salts are the normal phosphate {blue} CrPO4, can be hydrated; sodium carbonate solution produces a similar precipitate to hydroxide that may be a basic carbonate or Cr2(CO3)2.xH2O. The color is purple – Cr[III] also produces CO2 complexes.

Correction to Part 1 Above.

 ……sodium carbonate solution produces a similar precipitate to hydroxide that may be a basic carbonate or Cr2(CO3)2.xH2O. The color is purple – Cr[III] also produces CO2 complexes…..

I re-ran this one today and now find that the color quoted is nearer lavender or light blue gray. Nor does it dissolve in excess Na2CO3. A short boiling does not convert the color, except to maybe reduce the bluish tint to slightly more gray. Try it and see!

But it is *not* green as several texts have it. (But I have not yet tried the green form of the sulphate) All texts also say this is not a carbonate but a hydroxide and on further effort I tend to agree. If the precipitate is washed many times with water, to eliminate carbonate contamination, and treated with acid, very little CO2 is evolved. It dissolves to give the violet form of Cr[III]+++ aqua complex.

I think the difference in color is probably due to crystal size, a frequent cause of such phenomena. As for CO2 complexes, this too is ruled out. I think this is a Der Alte aberration; I must have been thinking of the carbonyl, Cr(CO)6.

Remembering that the (violet) ion is [Cr(H2O)6]+++ and is acidic, we have in water

[Cr(H2O)6]+++(aq) + H2O(liq) < -- > [Cr(H2O)5(OH)]++(aq) + H3O+(aq);

So one would expect Na2CO3 + Cr+++ salt to produce CO2 provided the pH is low enough. It does (best seen in conc. Cr salt solution, else the CO2 remains dissolved). As the salt is gradually neutralized by OH- ions from the dissolved Na2CO3 or NaOH a sequence of exchanges between the H2O ligands and the OH- ligands can be assumed to take place:

[Cr(H2O)6]+++(aq) => [Cr(OH)(H2O)5]++(aq) => [Cr(OH)2(H2O)4]+(aq)

=> [Cr(OH)3 (H2O)3] (Solid precipitate);

And if the pH exceeds ~11 afforded by Na2CO3 in solution, as in the case of NaOH solution, this precipitate dissolves to form negative aqua complex ions:

=> [Cr(OH)4(H2O)2] - => [Cr(OH)5(H2O)] - - => [Cr(OH)6] - - -

as the pH goes from 11+ to 14+.

Whether the so-called chromites like NaCrO2 really exist I do not know. *Mellor* has:

“...when hydrated chromic oxide is treated with sodium hydroxide, the formation of chromite precedes the formation of the hydroxide. With sodium hydroxide below 102V, primary sodium chromite is formed, whilst above 102V the soln. contains also tertiary sodium chromite. Potassium chromite is similarly produced ; below 82V-alkali only the primary chromite is formed, whilst above 82V the soln. contains also secondary chromite. From soln. of potassium chromite which have stood for a long time, needle-shaped crystals of the formulaCr2O3.3K2O.8H2O have been obtained.”

(V stands for the inverse of concentration, liters/mol, IIRC). Best of luck if you want to try it!

The precipitated hydroxide aqua complex does dissolve in strong NH3 solution, in spite of its weakness as an alkali. It switches water for NH3 in the hexa coordinated complex,

[Cr(H2O)6]+++ + 6NH3 => [Cr(NH3)6]+++ + 6H2O etc.

For such beauties as Hexaamminechromium (III) Chloride, etc., see *Brauer* – you are on your own.

The overall message is that Cr[III] preferentially forms hexa-coordinated compounds, ionic and covalent, unless anhydrous. And anhydrous CrCl3, eg, is insoluble if pure – and covalent.

I performed the original experiments over a few months last year. These notes come from that record.

Chromium Revisited – Part II

A bit more about Cr2O3 and Cr(OH)3:

In the first part of this series the attention was paid to Cr[III] compounds and a few of their complexes. The most stable form of Chromium under normal conditions is in fact Cr2O3 which to my surprise has a higher heat of formation (lower enthalpy) than even the fluoride (that entropy term at work, no doubt!). Again I am severely tempted to add a Pourbaix diagram at this point, but again I resist for two reasons; one, it may confuse and two, I cannot find a suitable simple one at the 1M Cr+++ concentration indicative of typical experimental conditions. For those familiar with the Eo/pH diagrams, the one in Wiki under Chromium can be consulted, but it is for 10^-5M Cr+++ concentration. Change of concentration changes the position of vertical boundaries especially but moves all boundaries except, of course, the (dashed) water lines.

You will, for instance, never see Cr(OH)3 on Pourbaix diagrams (OK, I wouldn’t bet on it) because they show the most thermodynamically stable form under the Eo and pH condition of the axes at STP. That is Cr2O3; it covers a wide area.

2Cr(OH)3 -- > Cr2O3 + 3H2O + 2.13E05 j/mole

(see [www.argentumsolutions.com/publications/CorrVol39p4881983.pdf](http://www.argentumsolutions.com/publications/CorrVol39p4881983.pdf)for a discussion of issues re Eo/pH diags for Cr/water: it has several but they cannot be copied – secured pdf)

In other words, CR(OH)3 is metastable at RT and the equilibrium lies well to the right in the above equation. You can show this experimentally as follows. {There, I knew I ought never to have mentioned Pourbaix diagrams….}

(4e) This takes a bit of time to carry out. One must first produce a working quantity of Cr2(OH)3.xH2O from a Cr+++ compound as outlined previously – aim to get 5-10 g reckoned as unhydrated. Wash copiously with water several times. The let settle and decant, finally filtering through a fine mesh filter paper. Dry carefully in an oven at ~ 120-140C for several hours, until the mud becomes a powder of a dull green color.

Try reacting some of this with dilute acid – it should react fairly rapidly and give the violet form of the Cr[III] salt. Scrape the powder from the filter paper and place in an evaporating dish and heat in the oven to around 250C. This still does not totally dehydrate the hydroxide but also does not seriously convert it to oxide. This can be proven by reaction with acid or strong alkali. Now take the powder and heat slowly on an iron spoon over a propane flame. Somewhere around a dull red heat (500-600C, I would guess) if you are lucky you may see it caloresce – suddenly brighten and then dim. {This did not work the first time I tried it – it needs a fair quantity (at least 5g) to work, IMHO}. Now heat strongly. On cooling the power still has a dull green color but it almost totally non-reactive to strong acid or alkali solutions, showing that Cr2O3 is very unreactive.

The experiment demonstrates that Cr(OH)3 is changed to the oxide by heating strongly enough, but is not exactly unstable. In fact it can be kept indefinitely at RT in the dried state without losing reactivity. The calorescence is probably due to a change of state (entropy change) as the amorphous structure left on ignition of the hydroxide changes to crystalline Cr2O3 at some transition temperature..

Other ways to make chromic oxide are to heat ammonium dichromate (NH4)2Cr2O7 or K2Cr2O7 with sulphur. Both ways tend to produce a bright green product, especially the second (which is fun to perform!).

 (NH4)2Cr2O7 -- > N2 + 2H2O + Cr2O3

K2Cr2O7 + S - -> K2SO4 + Cr2O3

 (4d)Heat some solid potassium hydroxide (or NaOH) with about the same quantity of potassium nitrate (or NaNO3; chlorates can be used) in a nickel (or SS) crucible or dish until melted together. Add some Cr2O3 made by one of the above methods or otherwise available. It reacts to produce Chromate, K2Cr2O4, a yellow substance. The Cr[III] state is oxidized to the Cr[VI] state easily under the extreme alkaline conditions – even air will do this, slowly. More of this later.

It is worth noting that Chromium is quite a reactive metal, slightly less so than Zinc but more so than iron, yet chromium is plated on to iron (over Ni or Cu) and is very resistant to corrosion. This is believed to be because of Cr2O3 formation. The metal does dissolve in fairly dilute HCl but nitric acid passivates it, and sulphuric also has little effect, and even when concentrated has to be heated to react with any speed.

Chromium Revisited – Part IIIa

IUPAC Gold Book defines a transition element as one whose atom has an incomplete d sub-shell, or *which can give rise to cations with an incomplete d sub-shell*]. The electronic structure of Cr in the ground (unionized gaseous) state is [Ar].3d5.4s1; it has six valence electrons outside the argon electron structure.

For technical reasons (as the physicists are wont to say whenever the explanation is too involved in a cloud of Quantum Mechanics) the 4s level has a lower energy level than 3d in the atoms K, atomic number (Z) =19 and Ca Z=20. That is, 4s is bound more strongly to the nucleus. And hence the d levels are not occupied first. The simplified explanation is that electrons in the s orbitals penetrate the Ar shells and hence see a higher part of the nuclear charge, while the d orbitals do not. As Z increases the Ar core decreases in size due to the increased nuclear charge and the 4s levels begin to approach the 3d levels.

The first appearance of the 3d orbitals is at Sc, [Ar].3d1.4s2; past Zn, [Ar].3d10.4s2, the 3d and 4s shells are filled and the 4p subshell starts at Ga. At vanadium Z=23 the 4s and 3d levels approach equal energy, and at Cr Z=24 the 4s electron actually has a higher energy by 0.96 eV (*Pauling*). This means the 4s electron is lost first in compounds of Cr.

The 3d block elements have no chemically similar elements of lower atomic weight and represent a new series with new chemical properties. Neither zinc nor scandium ions have any colored compounds AFAIK (unless with transition metal anions, of course!) although they are part of the d block elements. They can form complexes, of course.

I don’t consider them true transition elements, only those from Ti to Cu. These elements form at least one chemically stable *ion* with a partly filled d sub-shell. The d orbitals can, due to the Pauli exclusion principle, each have two electrons with opposed spin, but the d shell first fills up each with only one in each, due to the fact this is the lowest energy state and these are parallel rather than opposed.

Ti has configuration [Ar].3d2.4s2, Cu has [Ar].3d10.4s1. But Cr does not follow the usual Building Rule (in German *Aufbau)* for the electronic configuration. Vanadium has [Ar].3d3.4s2 as expected but Cr has [Ar].3d5.4s1 instead of [Ar].3d4.4s2; the latter corresponds to an excited state of neutral Cr.

Past this point only MS or PhD students and researchers steeped in QM fog fear to tread; I certainly dare not. Things get complicated in a hurry with hybrid orbitals, splitting fields etc. that make the more familiar sp hybrids of the carbon atom look like child’s play.

The bottom line is that Cr is essentially hexavalent due to its five 3d’s and one 4s electron and the lone 4s is lost first on compound formation, but no Cr(I) oxidation state exists AFAIK. The states labelled Cr[0] (AFAIK) (except the metal, by definition) are all coordinated covalent compounds with organics like Cr(CO)6 and the structure is then 3d6. 4s0; Cr(II)++ is 3d4.4s0; Cr[III]+++ is 3d3.4s0 and so on.

 The complex formation so prevalent in Cr and other transition metals is explained by the Cr atom ion having vacant bonding orbitals that act as a Lewis acid. Suitable ligands that act as Lewis bases then donate electron pairs to form the bond eg **:NH3 or H2O:** or EDTA with its six sites.

The colors of Cr and true transitional compounds are due to transitions between levels of the d electrons which fall within the visual range 380nm to 750nm, or photons with energy 3.28 to 1.59eV.

Enough Preamble and on to the Chemistry.

Metallic Cr was mentioned above in Pt.1. We pass on to Cr[II] compounds.

**Chromium[II] compounds**

These are all strong reducing agents and hence can only be made by even stronger reducing agents. The fundamental equation is thus, using Cr[III] compounds as the Cr source, and ignoring aqua complexing on both ions,

Cr+++(aq) + e- -- > Cr++(aq) Eo = -0.42 V

This can be achieved electrolytically by cathodic reduction or chemically by dissolving metallic Cr in dilute acids or using the Zn/acid method. Electrolysis requires a divided cell. The acid solution needs Cr metal. The Zn/acid method is easier and quicker but introduces Zn salts into the solution.

Zn(s) -- > Zn++(aq) + 2 e-Eo = 0.782 V

So 2Cr+++(aq) + Zn(s) < --> 2Cr++(aq) + Zn++(aq) dE 0.386 V …overall reaction

However, if we look at the overall reaction as (sulphate case with H2SO4, Zn)

Cr2(SO4)3 +Zn -- > 2CrSO4 + ZnSO4, it looks as if adding acid is not necessary. But it is; so also

2H+(aq) + 2e- **- -** > H2(g) Eo=0.000V

Zn(*s*) + 2H+(*aq*) -- > Zn++(*aq*) + H2(*g*) Eo=0.782V

Hydrogen is formed as a by-product of the zinc-acid reaction but the reduction of Cr[+++] occurs on the surface of the Zn. Does this hydrogen also reduce Cr[III]?

{ *Herein lies the 200 year old mystery of the “nascent” hydrogen so popular in the ancient texts – still not properly solved AFAIK. If, instead of zinc you use iron, hydrogen is still produced but the Cr[III] is not reduced.*

*For Fe(s) -- > Fe++(aq) + 2e- Eo=0.44V: This is 0.02V higher than the Cr[III] to Cr[II] reduction potential potential so any effect would have a very low equilibrium constant K. Using electrochemical reasoning one does not expect reduction; K is too low. And so it turns out. Yet H2 is produced as usual and this H2 – in its “nascent” form – also cannot effect the reduction.*

*What is special about the “nascent’ form produced by Zn, compared with that produced by Fe, if it is in fact effecting the reduction?*

*It is almost certainly not produced as H + H -- >H2; the H-H bond strength is 436 kJ/mol or 436/94.5 eV = 4.6 eV and there is nothing energetic around powerful enough to achieve this energy. If the H2 does not enter the reaction why is the acid (source of H+ ions) needed? If it does, in what respect is it an excited form of hydrogen?*

*The texts merely produce hand-waving or sweep this one under the rug. Few will dare to even mention the stoichimetry of the Zn/acid reduction. This subject is well worth a thread on its own. If any of you theoreticians knows of interesting recent papers on this horny old problem I would be fascinated to read them!* }

As usual I ramble. One more point before I turn to the practical experiments. All the texts mutter about ‘instant oxidation by oxygen in the air’ and ‘Cr[II] are capable of reducing water to hydrogen’ and quote very elaborate precautions to avoid these calamities. Do not be put off! Yes, they occur:

4Cr2+ + O2 + 4H+ → 4Cr3+ + 2H2O dE = + 1.64 V … oxidation of Cr++

 2H+ + 2 e– → H2 Eo = 0.000 V

Cr3+ + e− → Cr2+ E0 = - 0.410 V

2 Cr2+ + 2H+ → H2 + 2Cr3+ d E = + 0.410 V …reduction of H+ in H2O

These are energetic, especially the oxidation, so air must be somehow excluded.

**Chromium Revisited – Part IIIa**

(5) **Chromium II Compounds.**

(5A) Reduction with zinc/acid.

This was mentioned above. To see the color of the Cr++ ion (hexahydrated) is quite simple. Take a long thin test-tube (longer and thinner the better) and load it half high with cleaned zinc foil or sheet (hammer out if necessary and use dilute acid to dissolve off oxide). The aim is to maximize the surface area of the zinc and minimize that of the liquid surface when filled. Dissolve some Cr[III] salt – chloride or sulphate {not saturated! Say 25g/100g}, chrome alum (saturated) etc. – in water to produce a deep green or violet solution. Fill the tube to about the top of the zinc. Little happens. Add conc. HCl (If using chloride) or 40% sulphuric acid in sufficient quantity to react with part of the zinc but not all (difficult to judge – add in stages). That way the final solution is not heavily acidic.

The usual zinc/acid reaction occurs. Plug the top of the tube with tightly rolled tissue paper, cotton wool or fine glass wool. This minimizes convected air entering the tube and tends to keep a hydrogen atmosphere above the liquid which improves efficiency. The liquid begins to get paler at first and violet (or green) turns to a clear sky to darker blue that is quite different as the Cr[II] develops. The color change is quite striking, especially with the green. Equations shown earlier.

The solution containing the Cr[II] can be kept for some time if poured off into a smaller test tube nearly full and tightly corked with a rubber bung, especially if refrigerated. I never managed to crystallize the Cr[II] salt out because the potassium sulphate or the zinc sulphate come out of solution first and you cannot boil to evaporate! In order to get the chromous salt in a pure state electrolysis of chromic salt (preferable sulphate) in a divided cell with Cr[III] in both anode and cathode compartments (when one can simultaneously produce (di)chromate at the anode!)

(5B) Instability of Cr[II] salts WRT water.

Take some of the solution from (5A) and heat in a test tube. Once it gets hot bubbles of H2 appear and on boiling the blue color reverts to green, showing that Cr[III] is produced by reduction of water.. Equations shown earlier.

(5C) Instability of Cr[II] salts WRT Oxygen (air).

Pour some of the liquid into a 50ml beaker and leave for a day or so. The solution reverts to the violet form of Cr[III].

(5D) *Chromium amalgam*, which can be made by electrolysis at an Hg cathode, is said to produce black CrO on oxidation in air. Have not tried this due to very short Hg supplies!

(5E) Chromous Acetate, Cr2(CH3CO2)4(H2O)2:

It can be made as a red solution by adding a reasonably strong solution of Zn reduced Cr[III] sulphate to a saturated solution of sodium acetate. With care, small red crystals can be made and kept. I used the following method:

Take a glass tube, 1 to 2 cms ID X 25 cms long or thereabouts and fit the lower end with a rubber bung and a short glass tube. Attach a short rubber/neoprene tube with a Mohr’s clip or a pinch cock to a longer glass tube. Prepare a saturated solution of sodium acetate in water and cool to around 5C in a refrigerator.

Using a suitable support, place the long tube vertically with a mat of glass wool next to the bung and fill with zinc pieces to a height of around 10-15 cms. Add a moderately strong solution of Cr2(SO4)3 (this is very soluble, don’t use a too concentrated solution) to the zinc with the Mohr’s clip in position. Add 40% or so H2SO4 and proceed with the reduction.

In this preparation chrome alum is undesirable because of the potassium content; potassium sulphate may crystallize out at a later stage. {If all your have is the alum, convert it to hydroxide and dissolve in sulphuric acid, which is the way I did it.}

Once the acid is consumed (there should be zinc remaining), run the solution into a Erlenmeyer flask containing the cooled sodium acetate by releasing the Mohr’s clip. The end of the lower glass tube should be under the surface of the acetate solution. The quantities should be such that the flask is nearly filled to the top with the incoming solution – a bit of prior experimentation can ensure this. The acetate should be in excess.

The blue solution entering should produce a yellow then a red coloration. Remove the glass tube and put a rubber bung on the flask. Crystals of the Cr[II] acetate may form immediately; if not they should on cooling in an ice mixture in a refrigerator. The color is brick red. After cooling for 12 Hrs, decant and rapidly dry between good quality filter papers. The red crystals can be kept some time in a small tube but will turn darker, then brownish and finally greenish due to oxidation and/or water reduction. If you have a dessicator, dry in that first (over conc. H2SO4).

(5F) Chromous Oxalate can be made by the same process and is also red. It is said to be less soluble and more stable than the acetate. In this case use the potassium salt because sodium oxalate is poorly soluble.

(5G) **Cr[II] Hydroxide.**

In the presence of the zinc from the reduction, addition of sodium hydroxide precipitates white zinc hydroxide which masks the yellow color of the Cr[II] compound. However, the production of Cr(OH)2 can be inferred by the fact that the solution becomes colorless and the precipitate is not pure white but yellowish. On standing the gray-green color of the Cr[III] hydroxide appears.

**Discussion of Cr[II] compounds.**

All these compounds are strong reducing agents and deteriorate in air due to oxidation. Nor are they stable in solution due to the ability to reduce water to H2 gas. As such they are laboratory curiosities and cannot be kept for long. They cannot be concentrated in solution by boiling since this accelerates the reduction. Apart from the acetate I have not managed to crystallize out any Cr[II] compound. The Ac is atypical with its red coloration and is both dimeric, covalent co-ordinated and non ionic (see Wiki). Most ionic acetates are very soluble but Cr[II]Ac2.H2O is sparingly so, although soluble in hot water (hence the cooling required above).

Anhydrous Cr[II] compounds can be made by the action of eg chlorine on Cr metal or oxide and carbon. They are white according to the texts, but the processes require very high temperatures.

The catalytic action of Cr[II] ions on insoluble Cr[III] compounds never fails to be mentioned in texts on Cr compounds so I might as well join the club. The explanation given is as follows: The Cr[III] compounds dissolve rapidly with a trace of Cr[II] ions by the following reduction chain reaction:

 Cr[III]X3(s) + Cr++(aq) -- > Cr++(aq) + 3X- + Cr+++(aq):

The Cr++ ion reduces the insoluble covalent Cr[III] compound to a new Cr++ ion, also soluble, and is oxidized to Cr+++, and so on. I guess the thermodynamics allows this.

**Chromium Revisited Part IV**

The current version of the Periodic table is in some respects less genuinely chemical in flavor than Mendeleef’s original, which he based on ‘higher saline oxides’ of the elements as representing the maximum valence state. The current version (IUPAC) stretches across 18 elements. If it included the 4f block [rare earths] it would stretch all the way across your wall! Elements exhibiting similarities due to valence are now widely separated.

Older versions placed oxygen and sulphur etc, as Group VI elements along with Cr and Mo, etc., in VIa and VIb sub-groups. Between S and Cr there are, in fact, distinct similarities such as SO2Cl2 and CrO2Cl2, or chromates and sulphates, CrO3 and SO3 and so on. Mendeleef also noted the sideways similarities such as those between V, Cr and Mn. By such means he was able to predict unknown elements yet to be discovered.

**Chromates**

Comparing the lower oxidation states of Mn and Cr, we can note that with Mn the Mn[III] compounds are powerful oxidants whereas Mn[II] is stable. With Cr, Cr[II] is a good reducing agent whilst Cr[III] is the stable state. Permanganates are considerably more powerful oxidants than Chromates:

Acidic at pH=0: MnO4- -- > Mn++ , Eo = 1.51v; Cr2O7- - -- > Cr3+++, Eo=1.38V;

at pH=14, MnO4- -- > Mn(OH)2, Eo= 0.34V and CrO4- - -- > Cr(OH)3, Eo= -0.11V

and if the hydroxide is ‘redissolved’ in the alkali, forming the chromite ion,

CrO4- - -- > Cr(OH)4- with Eo = -0.72V

As a consequence chromates can be easily made in the wet way unlike permanganates (see the long permanganate thread or get mnOXY.doc from scipics). Suitable oxidants to take the Cr from [III] to Cr[VI] state are hydrogen peroxide (acidic or alkaline) or NaOCl (alkaline only).

(6a) Under approximately neutral conditions:

Starting from a Cr[III] salt, precipitate Cr(OH)3 as above. Add H2O2 (3% is OK, it is around 1N). The greenish precipitate dissolves and the solution turns yellowish due to formation of chromate ion:

2Cr(OH)3 + 3H2O2 + 4OH- -- > 2CrO4- - + 8 H2O

Notice that for neutrality 4 positive ions must be present in the above. If only water is present initially then a solution with H+ ions would have to result, implying a solution of chromic acid. However, if instead we make the solution alkaline with , say, NaOH, then sodium chromate results, so long as the final solution is near neutrality or alkaline. Which leads us directly to:

(6b) Produce a solution of the green ‘chromite’ by carefully redissolving the precipitate in NaOH. Add H2O2 (or NaOCl solution) slowly until the solution is bright yellow:

Cr(OH)3(s) + OH- -- > Cr(OH)4-(aq) ….. green

Cr(OH)4-(aq) + 3H2O2 + 2OH- -- > CrO4- - (aq) + 8H2O …… yellow

(6c) Alkaline hypochlorite (bleach is about 0.8N at 6%) can be used to make sodium chromate equally well:

CrCl3 + 2NaOCl + 6NaOH -- > Na2CrO4 + 3H2O + 5 NaCl

Any Cr[III] salt can be used in place of the chloride, and H2O2 used instead of hypochlorite, or potassium salts used instead. Na2CrO4 is quite soluble (85g/100g aq at RT) but using the above method does make the extraction and purification somewhat difficult due to the preponderance of NaCl. Cr2(SO4)3 and H2O2 as oxidant is a bit easier (I’ll leave it to you to work out the equation!).

(6d) Neutralize the yellow solution produced in (6c) to slightly acidic with acid. The solution turns orange due to formation of dichromate:

2CrO4-- + 2H+ -- > Cr2O7- - + H2O; at pH ~ < 5.9 and this can be reversed:

Cr2O7- - + 2OH- -- > 2CrO4- - + H2O at pH > ~ 6.7

Dichromates are still in oxidation state [VI]; this is a distinct difference from manganates, where the oxidation state varies from [V] in the hypo- , [VI] in the manganate and [VII] in the permanganates.

The structure of the chromate ion is (-O)(O)Cr(O)(O-) and that of the dichromate can be written as (-O3)Cr-O-Cr(O3-). Further addition of CrO3 groups is possible to produce polychromates M2CrO4(CrO3)n, all in oxidation state Cr[VI], which tend to be marginally stable. Treating K2Cr2O7 with concentrated nitric acid is said to produce a trichromate K2Cr3O(10) - (haven’t tried this).

Many chromates are insoluble. K, Na, Mg and Ca are all soluble to some extent. Most chromates are yellow, but Ag, Hg are red; most dichromates red to reddish brown and tend to be more soluble than the chromates.

Treating a chromate or dichromate with H2O2 causes a transient blue solution (due to the formation of CrO(O2)2 (Wiki)). This is a very sensitive test for chromate or dichromate.

A final reminder that all chromates and Cr[VI] compounds are fairly poisonous. Although Cr[III] compounds are only marginally so, chromates are because of their oxidation capabilities and are also carcinogenic; they stain and can be absorbed through the skin. Wear gloves and watch eyes. They are not usually an environmental hazard because of ready conversion to Cr[III] state, except in very acidic waters.

**More on Chromates I**

(7a) **Preparation of Chromates from Cr+++ salts.**

Unlike with Manganates, the Chromates all represent the single oxidation state Cr[VI]. Dichromate is stable only as solid or in acid solution and can be considered as a condensation product of the chromate ion. Further condensations to the poly chromates are possible. Neither of the acids H2CrO4 or H2CrO7 can be isolated although there is good evidence for the existence of the ion HCrO4-; however, hydrogen acid salts of Cr also do not stably exist.

As shown before, chromates are readily converted to dichromates and hence only one species need be considered. If the other is wanted then either a suitable acid or alkali can be used to make it simply.

**Remember that all Cr[VI] compounds are poisonous. Wear gloves; do not breath in vapors when evaporating**

For several reasons the oxidant H2O2, which might seem ideal as its only product is water, was found to be unsuited to this purpose. For a start it has a tendency to decompose to O2 in the presence of heavy metal ions; and Cr+++ is no exception. In acid solutions with Cr+++ ions present it has a tendency to produce peroxy compounds which are unstable; these decompose with evolution of O2. In ‘neutral’ (unacidified) solutions O2 is also produced (the solutions are actually acidic). In alkaline solutions, depending upon the order of mixing of components, the hydroxide may be precipitated and the reaction is then slow; also peculiar products seem to be formed as intermediates (See later on this).

The net result is that no sensible stoichimetric equation can be written for the action of H2O2 on the Cr+++ ion in solution; it depends upon exact conditions such as concentration, temperature, pH and just possibly phase of the moon! It is inefficient. Another Oxidant is needed. I wasted a lot of effort on this possible method, concentrating H2O2 etc. (There’s a good thread in SciMad on H2O2 concentration, should you want to do it).

So I turned to the old favorite (and cheap!) sodium hypochlorite. This is unstable in acidic solution, producing chlorine, oxygen, or a combination, depending on acid. Hence attention is directed to alkaline solutions where chromate will be the product.

A putative oxidation in ionic terms might be written:

2Cr+++(aq) + 3OCl-(aq) + 10OH-(aq) -- > 2CrO4- -(aq) + 3Cl-(aq) + 5H2O …(1)

 Violet (or green) -- > Yellow

However, if solutions containing these ions were mixed, since ionic reactions are (nearly) always faster than oxidations because the bond in the oxidant has to be broken, and the hydroxide is predominant, the likely result would be a large amount of gelatinous hydroxide, especially if concentrated solutions are involved, giving a modified equation in which the precipitated hydroxide is oxidized:

2Cr(OH)3(s) + 3OCl-(aq) + 4OH- (aq) -- > 2CrO4- -(aq) + 3Cl-(aq) + 5H2O …(2)

 Green-gray ppt. + Colorless liquid -- > Yellow liquid

It is best to slowly add a combined solution of hypochlorite and hydroxide gradually to the Cr+++ ionic solution stirring if necessary to avoid a mess of Cr(OH)3 forming. An alternative method (one I favor) is to pre-precipitate the hydroxide and just redissolve it, then adding the NaOH dissolved in the NaClO solution:

2Cr(OH)4-(aq) + 3OCl-(aq) + 3OH- (aq) -- > 2CrO4- -(aq) + 3Cl-(aq) + 5H2O …(3)

 Green -- > Yellow.

The overall reaction using Na+ and SO4- - as spectator ions can then be indicated as:

Cr2(SO4)3 + 3NaOCl + 10NaOH -- > 2Na2CrO4 + 3Na2SO4 + 3NaCl + 5H2O …(4)

I prefer this on principle to using Cr[III] chloride for reasons discussed below. A very small excess of NaOH is desirable to keep the solution alkaline (> ~pH 8). The color change serves as a weak indicator (the reaction is not reversible).

Stirring helps during the additions; certain peculiar side reactions which do not seem to radically affect the product may also occur. *Do not use highly concentrated solutions* – the chromic sulphate is extremely soluble – or you will land up with an intractable mess. 5% Hypochlorite is a good strength (e.g., bleach).

If chromic chloride is used, 9mols of NaCl is produced for every 2 of chromate which renders extraction difficult. Do not use KOH in place of NaOH or it will confuse the products more than necessary.

The solubilities of the various products (g/100g Aq.) are ~ as follows: (Wiki)

Compound Temp C = 0 30 60 100

Na2CrO4 32 88 115 126

Na2SO4 5 41 45 43

NaCl 36 36 37 39

The relative weights of expected products are Chromate, 1.00; Sulphate, 1.58; Chloride, 0.65. Because of the common ion effect (Na+), actual solubilities will be somewhat less than above; how much less we cannot calculate. What strategy should be used to isolate the chromate? First estimate how much water would dissolve each component, assuming no common ion. This is proportional to mass and inversely proportional to solubility; in the same order as above, the ratios are @100C are roughly, 0.793 : 3.67 : 1.67 . At 0C ratios are: 3.13 : 31.6 : 1.81.

The strategy becomes obvious. (a) Evaporate @ ~ 100C until crystals appear. At this point the sulphate is saturated. On cooling to 0C most of the sulphate will precipitate. (Be careful about supersaturation of the sulphate; it’s about the worst offender I know).

Those familiar with fractional crystallizations know how to proceed from then on. Some hate the process; I revel in it. It takes a lot of time and patience. To avoid the massive task of actually crystallizing out the chromate, after eliminating as much NaCl as possible (important!), we pull an ace out of our sleeve. We convert to dichromate by adding one equivalent of sulphuric acid:

2Na2CrO4 + H2SO4 -- > Na2Cr2O7 + Na2SO4 + H2O

Now the sodium dichromate is incredibly soluble – 163g/100 aq. @ 0C and 417 g/100g @100C – no way that is going to precipitate while you get rid of more sulphate by the same process as the chromate. So you land up with a strong solution of Na2Cr2O7 plus minor amounts of chloride and sulphate.

The reason for keeping the chloride level as low as possible is that HCl may be generated if you let the acid level get too high. If you use appropriate amounts this will not happen, but it requires careful measurements. With strong acid dichromate may form chlorine or, worse, CrO2Cl2. The latter is unlikely and even if formed will hydrolyze. See later.

Finally, the dichromate is precipitated by the addition of a potassium salt (not sulphate).

The solubility of K2Cr2O7 is far less than the sodium salt and it separates on cooling to 0C. Solubility @0C, about 5g/100; @ 30C, 18g/100; @ 60C 46g/100; and @ 100C, ~80g/100

The ammonium salt is also far less soluble and can be similarly produced. Solubility is around 18g/100g @0C. Do not boil a solution containing ammonium dichromate, it will decompose. The color of this dichromate is orange.

The above wet method is a bit time consuming. The following fusion method is easy and recommended. It is much easier than the corresponding permanganate production.

**(7a) Preparation of Chromate from Cr2O3 or Cr(OH)3.3H2O by fusion**

 **Warning: Take care with fused hydroxides and nitrates. Use stable apparatus and do not perform in a dwelling area.**

Use a nickel, iron or SS crucible, small cup or bowl for this process. Do not use porcelain. The generalized reaction sought is as follows, Cr2O3 + 4MOH + 3[O] -- > 2M2CrO4 + 2H2O ;

M = Na or K; the [O] to be provided by a suitable oxidant.

O2 from air can be used but takes a very long time unless sparged through the melt. The Cr2O3 can be replaced by dried hydroxide Cr(OH)3.3H2O which decomposes to Cr2O3 at around the temperature of the melt. Suitable oxidants are nitrate, chlorate or perchlorate, the last needing a slightly higher temperature. Chromate is stable up to around 900C AFAIK so heating to bright red heat does not destroy it, although dichromate will not survive.

If MNO3 is used as oxidant, a proportion Cr2O3 : MOH : MNO3 of 1:1:1 by weight is good for M=K and 3:2:2 for Na, but add a little extra MOH to account for impurities such as carbonate.

The nitrate/hydroxide mixture melts at temps. between 200-300C, lower for the K salts. The time taken to complete the reaction depends on the nature of the Cr2O3 – if gritty it takes longer. If chromic hydroxide is used it must be dried and/or at least partially decomposed to oxide, to avoid splattering as it is added to the fused mixture. Pre-recalescent dried oxide/hydroxide reacts very much faster than technical Cr2O3 from pottery stores or oxide that has been strongly heated.

The reaction hoped for is 5Cr2O3 + 14K0H + 6KNO3 -- > 10K2CrO4 + 7H2O + 3N2

Steam and gas are emitted and the material may bubble so allow room for this in the crucible. The reactants will go pasty after ~15 minutes and should be stirred with a thick iron wire like a coat hanger. When the product becomes almost solid, increase the heat to a low red heat preferably with a cover over the crucible. (The nitrite first formed tends to decrepitate). Chromate is stable to about 900C so heating will not destroy it.

About 45 mins at a red heat is sufficient to complete the reaction. It is far easier than the manganate fusions and the yield is generally very good. Leach out the contents of the crucible after cooling. The main impurity will be KOH – the nitrate should have been fully decomposed. K2CrO4 will easily crystallize out as small anhydrous yellow crystals on filtering leach water and evaporation.

You can use ordinary filter paper with chromate but not with acidified dichromate. Sodium chromate will contain water of crystallization. Both chromates are hygroscopic or deliquescent.

It is said that K2CO3 can be used in place of KOH but I haven’t tried it. The carbonate is not easily fused, nor does it form a useful eutectic with nitrate.

**(7c)Dichromate to Chromate conversion**.

This can be conveniently done using carbonates instead of hydroxide. Boil to remove the CO2:

M2Cr2O7 + M2CO3 -- >2M2CrO4 + CO2; M=Na or K

**More on Chromates II**

[b](7d)Cr2O7- - to Cr+++ Reduction using alcohols[/b]

Since Potassium Dichromate is a more common compound than any Cr[III] salt, the experiments with Cr+++ described can be done in reverse by reducing dichromate to produce the sulphate (as chrome alum). This demonstrates the oxidation power of acidified dichromate, which is moderate. Chromate is a poor oxidant.

You can use ethanol or isopropyl alcohol. With C2H5OH, acetaldehyde is first produced but this may be further oxidized to acetic acid unless the aldehyde is expelled by heating. Isopropyl alcohol, being a secondary alcohol, produces a ketone, acetone, resistant to further oxidation. (Tertiary alcohols cannot be oxidized by dichromate). Hence, since we don’t want involatile acetates, use isopropyl and boil off the acetone (or condense it and use it!).

2(CH3)(CH3)COH +{O} -- > 2CH3(CO)CH3 + H2O

CR2O7- - + 8H+ -- > 2Cr+++ + 4H2O + 3{O}

The H+ comes from the sulphuric acid which also provides sulphate ions; the dichromate provides three {O} moieties for oxidation of the alcohol, and the potassium provides the other base in the alum KCr(SO4)2.12H2O as the final product. The Cr can be isolated as hydroxide if so desired and used to produce any Cr+++ salt with a suitable acid.

Dichromate is frequently used in organic chemistry as a moderate oxidant, but has no use in pyrotechnics AFAIK. Potassium dichromate crystallizes well giving large deep red or garnet crystals and is a favorite with crystal enthusiasts.

Ammonium Dichromate auto-reduces to a lovely green form of Cr2O3. It can be set off by a red hot wire or a match.

(NH4)2Cr2O7 (heat>200C) -- > Cr2O3 + 4H2O + N2.

Heating Potassium dichromate with sulphur also gives the same product:

K2Cr2O7 + S + heat -- > Cr2O3 + K2SO4 (or something like that).

**More on Chromium[VI]**

The following experiments are potentially **DANGEROUS. Take note of the hazards and act accordingly.**

**(7e) Chromyl Chloride, CrO2Cl2**

***{Not for k3wls; or even intelligent but over enthusiastic teens below the age of reason without knowledgeable adult supervision, or the cack-handed or panic prone. All those attempting ought to have had experience managing at least one previous disaster.}***

This liquid (bp 117C) is the acid anhydride of chromic acid, a Cr[VI] compound. It is an example of a volatile chromium compound at near RT. CrO2Cl2 is relatively easy to prepare. It is a deep red liquid, fumes in moist air due to hydrolysis, and has a vapor pressure of about 25 mm Hg at 25C (IIRC). It is definitely quite volatile. It has a very nasty acrid smell, vaguely like Cl2 or Br; the liquid is quite similar to Br in appearance.

**HAZARD: very poisonous vapor, about as bad as phosgene. As a bonus, it not only destroys lung tissue but deposits carcinogenic Cr if you survive.** However, it stinks so badly you will know it is deadly and receive a prior warning!

Do not perform this within the confines of any dwelling house or in any apartment block. Escaped vapor can hang around for a long time and leave its odor. **The only safe conditions** are in a proper lab under a fume hood with a good ventilation, or outside. Outside, use a fan to keep up a current of air toward the apparatus and away from the operator or any spectator. It also involves the use of concentrated H2SO4; familiarity of handling this is essential.

All glass apparatus is virtually essential. {Over 50 years ago my father and I used a retort with a long neck thrust well into an RB flask cooled by flowing water at a few degrees above freezing. Even so the smell of the stuff hung around our small private lab for days.}

Use a RB flask (a distilling flask with side tube would be best) with a dropping funnel to pour in concentrated acid slowly and attach a condenser to the tube from the flask. Lead into an ice cooled receiver flask with an arrangement to vent gases (HCl) and prevent ingress of moisture. Use no rubber or plastic tube connections except PTFE.

Do not attempt in an open test tube! I did do a very small scale effort to remind me last year, mixing by containing the acid in a small tube lowered carefully into a larger one, but I suggest you *not* try this.

Grind together about 5 parts common salt and 8 parts of potassium dichromate. The salt should be dried first by heating. Place in the flask with a dropping funnel containing a shut off e.g. a separating funnel. Fill the latter with concentrated acid (c 98%). Allow slow entry of acid, drop by drop. Excess acid beyond the stoichimetric proportion is needed as a dehydrating agent to prevent hydrolysis.

The reaction is firstly between the sulphuric acid and the salt to produce HCl:

 NaCl + H2SO4 -- > NaHSO4 + HCl

The reaction is immediate and rapid at normal RT. Reddish fumes appear as the dichromate undergoes partial reduction to Chromyl Chloride as the HCl is oxidized:

K2Cr2O7 + 4HCl + H2SO4 -- > 2CrO2Cl2 + 3H2O + K2SO4

Excess H2SO4 prevents hydrolysis. Heat is evolved but in the latter stages a gentle heat will be needed to distill off the remaining Chromyl Chloride. The product in the receiving flask is a very dark red liquid. It will probably contain dissolved HCl, removable by further distillation (if you so desire).

 It is not of much use and potentially dangerous. Although it could be kept as a trophy chemical by those so inclined, I am not sure of its stability long term for inclusion in an sealed ampoule. Sunlight (UV) is said to decompose it.

CrO2Cl2 hydrolyzes readily in water, and hence fumes in moist air, forming HCl and a solution of H2CrO4 = CrO3 + H2O: CrO2Cl2 + 2H2O < -- > 2HCl + H2CrO4

It is a strong oxidant and chlorinating agent. Great care must be taken not to let it get on the skin or serious burns result.

**(7e) Potassium Chlorochromate, KCrO2Cl**

A stable salt, potassium chlorochromate, KCrO2Cl can be made by adding concentrated KCl solution to chromyl chloride. It has a bright orange color & is stable if kept dry.

CrO2Cl2 + KCl + H2O -- > KCrO3Cl + 2HCl.

Alternately this salt can be made without chromyl chloride as follows:

Grind up 10g potassium dichromate heating gently if necessary until dissolved and digest with about 25 ml of 38% HCl solution. Filter through glass wool. Large red prisms of the chlorochromate develop slowly on standing, preferably at near 0C; keep in a refrigerator in ice/water for a day or so. (NOT, of course, one used for food!). Pour off the liquid and dry crystals on a porous plate (eg, terra cotta from gardening supplies; it is an strong oxidizing/chlorinating agent and destroys filter paper). It can be dried carefully in a stream of heated dry air, but too much heat causes release of chlorine. It hydrolyzes slowly if damp and is hygroscopic: K2Cr2O7 + 2HCl < -- > 2KCrO3Cl + H2O

**(7e) Chromium Trioxide CrO3**

**Hazard: Hot concentrated Sulphuric Acid. Powerful Oxidizing agent**

This oxide can be produced by, essentially, dehydrating a solution of chromic acid with concentrated sulphuric acid:

K2Cr2O7 + H2SO4 --> K2SO4 + ‘H2CrO4’ -- > K2SO4 + H2O + CrO3

The operation is rather tricky, in my experience, and yields tend to be disappointing. The problem, on investigation of the literature, seems to be due to the fact that CrO3 is least soluble in about 75% acid and one should aim for this percentage as an end point for good results. Weaker or stronger acid dissolves more CrO3. Unfortunately a diligent search of the web yielded no more precise data than this. Various sources quote the optimum as 66-85%. What the actual solubility is I do not know.

Further problems are the precipitation of K2SO4 at the same time; the extreme hygroscopic nature of CrO3 once precipitated and its strong oxidizing power. The CrO3 cannot be dried with any of the usual organic solvents – for instance, it will set fire to ethanol with incandescence. Since the solvent is sulphuric acid, the usual desiccators are useless. Suction from a Buchner funnel on a glass mat is the best that can be done. However, it can be redissolved in water and purified by careful evaporation/crystallization.. The solubility is about 62 to 65% by weight (185g/100g aq) over 0-90C.

At the level of acid needed the K2SO4 will exist as KHSO4: 75% acid is about H2SO4 + 2H2O. The solubility is then less than 10g/100 solution at 0C. With care, KHSO4 can be precipitated before CrO3.

The following method is copied from an old source: (quantities reduced)

“Dissolve 100g K2Cr2O7 in 160ml of hot water (temp has to be >80C for this) and add 135ml conc. H2SO4 very slowly and cautiously with active stirring. Stand over night in a cool place and next day decant solution off the potassium sulphate precipitate formed. Heat solution to 90C and add 50ml H2SO4; if a ppt. of CrO3 forms, add just enough water to re-dissolve. Evaporate till crystals appear and let stand for a day in a cool place. Collect and evaporate the solution for a further crop. Drain and wash with 15ml HNO3 (sg 1.46), then with a further 7.5ml. Dry on a sand bath.”

I used about the same procedure except for the HNO3, which I didn’t possess, re-crystallizing instead. It works but yield is only around 50% after re-crystallization.

I have not tried sodium dichromate but its easy solubility makes the following process sounds attractive. Adding conc. acid to a solution near 90C is a bit hairy!

“CHROMIC ANHYDRIDE, CrO3

The addition of sulphuric acid to a solution of either a chromate or a dichromate liberates chromic acid which is very soluble and can exist in solution in the different forms, H2Cr04, H2Cr207 and CrO3, in equilibrium with each other. With the addition of a large excess of concentrated H2SO4, water is withdrawn from the hydrated forms and the anhydride separates in the shape of red needles.

*Materials:* sodium dichromate, Na2Cr2O7-2H2O, 100 grams = 0.33 F.W.

36N H2SO4, 400 cc

*Apparatus:* 8-inch porcelain dish. Glass plate to cover the 8-inch dish, suction filter with glass marble, glass-stoppered sample bottle, tripod. Bunsen burner.

*Procedure:* Dissolve the 100 grams of sodium dichromate in 250 cc. of water and filter from any sediment. Add rather slowly with constant stirring about half of the concentrated sulphuric acid until a slight permanent precipitate of CrO3 is formed. Let the mixture cool for half an hour or longer, then add slowly, while stirring, the rest of the sulphuric acid. Let the mixture stand over night covered with a glass plate in order that the crystal meal may become somewhat coarser. In such a crystal meal standing in its saturated solution, the smaller grains dissolve and their material deposits out on the larger crystals. But even now the crystal meal will be rather fine and it will at first run through the filter; if, however, while waiting, the mixture is heated with stirring to 100° and allowed to cool slowly, and this process is repeated once or twice, a more satisfactory product will be obtained.

To collect the crystals, use a suction filter, but place a small glass marble in the funnel instead of the usual plate and paper. If the red crystals at first run past the sides of the marble, pour the liquid in the bottle repeatedly back on to the filter until finally the filtrate runs clear (see last sentence of Note 3 on page 5). After draining the crystals completely and pressing the surface with the round end of a test tube, stop the suction and pour 15 cc. of 16 *N* HN03 so as to wash down the sides of the funnel and cover the surface of the product. Stir up the product with this washing fluid for a depth of about 1/2inch. Suck dry and repeat the operation twice with 10 cc. of nitric acid each time. Finally drain the red crystals as free of liquid as possible, transfer the crystals to a dry 8-inch evaporating dish and place this on a hot plate to let the nitric acid evaporate. When the product is dry and no longer gives off vapors of nitric acid place it in the glass-stoppered sample bottle.”

(Blanchard, Phelan, & Davis, Synthetic Inorganic Chemistry; *fifth edition* 1936)

Re CrO3 also see <http://www.sciencemadness.org/talk/viewthread.php?tid=6116> esp. the post by S.C.Wack.

The similarity with SO3 is marked. Both tend to polymerize in long strings and produce wooly strands. The normal form of CrO3 is rhombic needles. Compare SO2Cl2 to CrO2Cl2 and the chromic acids H2Cr2O7/H2CrO4 with H2S2O7/H2SO4. The Cr2O7- - ion predominates at low pH; Ka for chromic acid is about 0.7 but the acid(s) are not isolable. As I said above, all this gets lost in the current periodic table

**Other Oxidation States of Chromium and comments**

This is a final wrap-up of this series (did I hear a sigh of relief?). Added for completeness, it is mainly a compilation of the literature searches I have done during the course of my Chromium madness phase. If I have actually done an experiment I have added an asterisk on this page.

**Correction:** Cr[II] compounds: Cr[II] oxalate, CrC2O4.H3O is a yellowish-green powder, not red as I stated previously, according to Brauer and CRC.

**Examples of other uncommon valences:**

**Cr[0]:** Chromium hexacarbonyl, Cr(CO)6, is a Cr[0] compound is solid at RT but potentially explosive on heating as are all carbonyls. Not made directly by passing Co over metal: difficult to make.

Brauer also cites a few metalo-organics of Cr[0], like Dibenzenechromium(0).

Brauer represents **Cr[I]** by Dibenzenechromium(I) Iodide, [(C6H6)2Cr]I, which I guess is valid by the usual rules.

**Cr[IV]:** Barium Orthochromate (IV), Ba2CrO4; obtained by a high temperature fusion (See Brauer) : BaCrO4 + Cr2O3 + 5Ba(OH)2 = > 3Ba2CrO4 + 5 H2O

**Cr[V]:** Potassium Tetraperoxochromate(V), K3CrO8, prepared from KOH, CrO3 and H2O2. Doable by an amateur. (See Brauer and Wiki)

 Another high temp fusion requiring especial conditions: Barium Chromate(V) (See Brauer)

 2BaCrO4 + BaCO3 => Ba3(CrO4)2 + CO2 + BaO2

*A side comment: The essential usefulness of Barium compounds means that every one remotely interested in experimental amateur inorganic chemistry should always have some on hand. It has quite unique properties for an alkaline earth element; eg. it will fix atmospheric oxygen as peroxide; its sulphate is about as insoluble as you can get; it has a fairly soluble hydroxide and it’s the only way I know of keeping a manganate ion stable.*

**The Oxides of Chromium**

Some are covered previously. (CrO, Cr2O3, CrO3): *vide supra.*

**Chromium[IV] Oxide (CrO2) and others**

All Chromium compounds AFAIK are paramagnetic due to unpaired 3d orbitals but CrO2 is actually ferromagnetic (consult a physics text for the difference, if necessary!). Hence you can use a physical test, since its magnetic susceptibility is very high. It was used for high quality audio recording prior to the digital era (remember Chromium tape?). Various ways of making it exist, most probably impure.

(1) Careful heating of CrO3 is said to produce distinct steps as oxygen is disengaged: (See Mellor on Chromium). The following have been reported but not all verified:

 CrO3 -- > Cr5O9 -- > Cr3O5 -- > Cr3O6-- > Cr5O13 -- > Cr5O12 -- > Cr6O15 -- > Cr2O3 as the temperature is raised from RT to 450C. (Note that Cr3O6 = 3CrO2).

Most of these – if they really exist – can be related to mixed oxides of the type [xCrO3, yCr2O3] or [xCrO2, yCr2O3] etc., i.e. Cr{III,VI} etc,, mixed oxides. Commercially Dupont produced the dioxide by decomposing chromium trioxide in the presence of water at a temperature of 800 K and a pressure of 200 MPa (Wiki) – obviously well outside amateur capability.

(2)\* CrO2 is alleged to be produced by heating chromic nitrate until all the nitric oxides are evolved. Since the nitrate can be easily be made from Cr[III] hydroxide plus dilute nitric acid, I tried evaporating a solution and gently heating it, whereupon a black solid remains that is, in fact, attracted to a magnet.

\*Another process I have tried is a sort of parallel to the disproportionation exhibited by manganese compounds – specifically the reaction of MnO4- with Mn++ ions which produces MnO2. For Chromium, any reaction between a chromate and a chromic or chromous ion sulphate might give what could be called potential Chrom(ous)(ic) (di)chromates. Such possible reactions total four, giving

Cr[II].Cr2O7 = Cr3O7; Cr[II].CrO4 = Cr2O4=2CrO2;

Cr[III]2.(Cr2O7)3 = Cr3O7; Cr[III]2.(CrO4)3 = Cr5O12

I did not try all of these but Cr[II] and CrO4- did give some blackish ppt., along with a heap of zinc hydroxide which obscured everything (from the reduction with Zinc). Results indeterminate!

Fluorides – Cr gives every valence from 2 to 6, as might be expected.

Sulphides *are not made with H2S*

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Enough; labor meus finitus est: I am done. But no -

**Chromium - Epilogue**

Don’t have any Chromium salts? Then use this CRUD method.

(CRUD = Chemical Reagent from Utter Dross, the art of producing reagents from household trash).

 Get some scrap stainless steel and dissolve in moderately concentrated HCl (~20-30%) (but not H2SO4 or HNO3, they will probably just passivate the SS), keeping metal in excess. Pour off liquid, evaporate to dryness but don’t overheat. Just dissolve the chlorides in water and add slowly a solution of 20% NaOH in bleach (5-6% NaOCl) – the Ni and Fe precipitate as oxides or hydroxides and the Cr gets converted to chromate. Let stand for a day, boil and decant and filter. Evaporate and crystallize out the Na chromate.

What? Don’t have any HCl? Then try the following, a true MadScience adventure into the absurd, a Der Alte special CRUD encore.

Fix up a crude electrolytic cell with a sacrificial SS anode and a cathode of carbon rods from old drycells. Add common salt, water and electrolyze. See if you can work out the rest…

Der Alte