

TO: E.P.A

FROM: James Rountree

Sellar  
Nobber  
Co. Meath

10<sup>th</sup> Dec 2012

RE: Change of status re light hazardous waste at Indaver Incinerator  
Carranstown, Duleek, Co. Meath and increase annual tonnage by  
20,000 tons.

E.P.A. Licence No. WO167-03

Dear Sir/Madam,

I enclose a copy of any submission to the Bord Pleanala Oral Hearing  
1<sup>st</sup> - 4<sup>th</sup> October last for your information. A considerable amount of the content  
is directly relevant to E.P.A. and represents further elaboration to my initial  
submission and a copy of this is already sent to you. Please consider all my  
submission to Bord Pleanala is also to be treated as a submission to E.P.A.  
There is a European Court judgement (referred to) that requires this

I am adamant that left over paint and paint rinsings must be recycled and I  
have been looking around for a high value product that could be produced from  
recycled paint "CHASIS BLACK" paint is a good possibility. It retails at over  
€100.00 for 5 litres. Specification is that it has a high oil content and never fully  
dries out. It will scratch but will not chip or flake. It is resistant to heat in a similar  
way to "radiator paint" and to all road environment splashes. It is a binary paint  
i.e. a potent anti-corrosion chemical is added before use and must be used within  
6 months of mixing. Uses are in the motor trade and industry. It is highly  
recommended as an under-body anti-rust treatment for motor vehicles and has  
good rust penetration characteristics. (If suitable filter-masks are not available, it  
must be applied by brush). Surfaces do not have to be perfectly clean, but they  
must be fully dried out and this includes flake rust that could in many respects act  
as a sponge for moisture.

11 DEC 2012

Signature: [Signature]  
Initials: AR

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Such a product would be an ideal outlet for paint recycling and there is scope for the promotion of a consumer friendly version for DIY motor vehicle and lawn mower, etc maintenance i.e. there is a currently unfulfilled market "niche" available but with the proviso that there are physical safety issues. A suitable ramp is needed with no jacks involved.

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On the issue of public health concerns about Incinerator emissions and Chromium in particular, Dr Martin Hogan from Employment Health Advisors Ltd. stated at the Oral Hearing that there are no concerns about Chromic Acid in the air at the low concentrations of Chromium emissions that the Indaver Incinerator at Duleek is producing. He said that the issue is "DOSE". Comparison of exposure on the factory floor with attendant staff health monitoring is an entirely different matter to exposure of the general public and his views are contentious. There is a serious question here and the public interest must be served.

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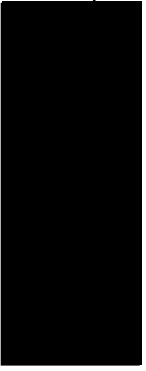
I enclose

1. Copy of submission to ABP Oral Hearing.
2. Photocopy of Text Book Chapter on Chromium.
3. Photo copy of reference (1950) from Encyclopaedia Britannica.
4. Copy of submission to ABP from Dr Hogan on behalf of Indaver for your information.

Please consider all material submitted by me for the Indaver licence revision.

Yours faithfully

JAMES ROUNDTREE



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Amendment to existing permission - Increase tonnage by 20,000 tons + incinerate "light, hazardous waste".

SUBMISSION  
FROM JAMES ROUNTREE  
SELLAR NOBBER  
CO. MEATH



My name is James Rountree. I am a dairy farmer living at Nobber, about 17 miles from the Indaver Plant. I have no qualifications in any field, but as a member of the public I am entitled to voice my concerns. I have a keen interest in health and a clean environment and you will note that I want to see various systems of gathering and analyzing health statistics compared on an ongoing basis. No one system should be depended on to the exclusion of others i.e. I want to see constant and continuous statical review with a variety of approaches because everyone knows that there are statistics and there are damned statistics. This is a serious matter of public confidence, evidenced by widespread subjective views that there is too much cancer, diabetes, asthma etc in the North East.

"I don't need to be an anthropologist to tell you that there is resignation and passive anxiety in the community and it is not there without reason, which of course should be inquired into, too. Indavers public relations flies in the face of this and is missing a very serious point that requires good social common arise.

Now, enough of that. We move on to an agriculture matter.

When a food scare arises there are two sections of the farming community. Those with the contamination problem proper and whose produce fails tests and the rest who need to guarantee that they do not have problem. To spot much a problem in the first place the Department of Agriculture and Food Safety Authority operate a SENTINEL POLICY and regularly test local produce but they do not observe one of the rules of environmental testing. (Anyone who says that food safety and environmental testing are separate issues is playing politics and flying in the face of public concern). The permission of the landowner and the reporting back directly of the detailed results is deficient and it is a rule of the proper recognition of environmental testing that the consent and subsequent information is available. This is something that needs to be discussed with the authorities. Question - who owns the information? It is very annoying that you can not see the laboratory certificate.

I.F.A. was advised to look for the establishment of a baseline study to help guarantee farm produce. This was good advice, but there is a problem that was not recognised at the time. Neither government or industry wants baseline study of farm produce because it interferes with the government/industry relationship. At earlier Oral Hearings I argued for an Agricultural baseline study. The authorities realised there were concerns but the baseline concept for farm

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produce was not taken on board and their was no improvement of the farmers position should a food scare arise i.e. dumping of produces and loss of income.

We do have a policy of traceability from farm level but it depends on confidence and it needs further development at processor and trader level. Even so, we are very proud of traceability systems, but market disruption is so much more extensive then a contamination problem proper.

So what is to be done? Technology has the answer. A good example is the DNA testing that now shows up spurious pork that is masquerading as Irish produce. Also, the African breed Zebu beef was shown up on sale in Irish restaurants. I think we must look to technology again so that any possible future food scare can be better managed.

I am putting forward a suggestion for discussion and consideration. We should have a scheme for graphing all undesirable chemicals and developed as a chemical fingerprint. If the stack output for sources of emissions is analysed and graphed and similar done for the other sources, a chemical analyst could review the produce graph and report the relative contributions of each of the emission sources and it does not matter that levels are below limit values, so everyone should have confidence in the system. Technology has developed to a stage now that accurate readings at very micro levels are possible and readings of levels that are regarded as being of no consequence would be a better guarantee than the agricultural baseline that was advised earlier. The DNA testing I referred to was a world first and this could be another world first marketing aid.

Currently many vegetables producers around Drogheda are being charged annual fees for laboratory testing by supermarket and wholesaler purchasers so that guarantees can be maintained that produce is free from contaminants. This is a good protection for the consumer. Co-Op and food processors also have their own laboratory facilities. Why not have a co-ordinated scheme? Who will lead it? We could have an Irish standard that no one else could match? And could you imagine what that would do for public confidence?

Finally, should dioxin, etc contamination ever arise, then government must order the party responsible to re-imburse members of the farming community whose incomes are affected (even if government decision is to have precautionary dumping), because if they do not, then the necessity for the fingerprint graph scheme I have outlined will be overwhelming. Also, in view of Indavers good reports of low dioxin emissions, they should have no problem agreeing to this and they do pay insurance premiums should an industrial accident ever happen.

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For the record, I am just an ordinary I.F.A. member who speaks on my own behalf and these are just my ideas on this subject. They arise out of personal concerns that I have.

Now, I want to speak about the contribution of E.P.A. to the planning process. So far, it has been minimal and I am speaking in the context of the European Court of Justice (ECJ Case C – 50/09 dated 3<sup>rd</sup> March 2011) regarding the separation of the planning process and environmental licensing.

This refers to failure by Ireland to "Correctly Transpose Article 3 of Directive 85/337 into Irish Law and procedures. The principal detail among others in the judgement is the separation of the planning and environmental licensing procedures. As I see it E.P.A. and Bord Pleanála have not "properly convened" for consideration of this application and perhaps this planning application may have to be repeated again with the necessary compliance with the judgement.

In this light it is very disturbing that the experience and expertise of E.P.A. is not directly available to Bord Pleanála regarding my next point about Cr VI which is believable when you consider that all the Cr VI compounds are derivatives of Cr O<sub>3</sub> Chromium tri-oxide and all contain oxygen. If you dissolve Cr O<sub>3</sub> you get Chromic Acid H<sub>2</sub> Cr O<sub>4</sub>, Cr VI does not arise in biological circumstances. Only under thermal treatment.

Chromates and Dichromate's are the principal chemical you would expect and they are the main problem – toxic and carcinogenic. They are analogous to sulfates i.e. similar in many respects and are frequently isomorphous to sulphates i.e. similar in many ways and interchangeable. Please refer to Wikipedia downloads attached.

My problem with the chromates and dic-chromates arises from a reference in the Ephraim textbook that seems to make them even more dangerous. Chromates and dichromate's in an uncontrolled situation are mixed and the relative quantities of each is pH dependant. According to the Ephraim text book, further acid will produce polychromates, which decay, when moisture is added to form di-chromates and free chromic acid.

The underlined paragraph in the Ephraim textbook says to me that with pre scrubbed incineration gases which contain a variety of acids, possible 15-20% water vapour and when there is a Chromium spike that polychromates are produced when you incinerate paint with Chromium pigments. This is dangerous and could compromise the health and life of individuals. Furthermore, as Chromium is a trace element in all materials of organic origin, there has to be a concern about all incineration.

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The situation has masked all long by environmental degradation of all Chromium VI compounds to Chromium III. Obviously there has been a variety of cascade reactions and the one I have just outlined is only one of them. And so, no evidence of a build - up of Chromium VI in the environment has ever been noted from incineration.

If I am right to any extent in my concerns there is a major oversight on the part of government and industry here which was masked by the environmental degradation of the Cr VI to Cr III and of course, the total Cr figure is all that is asked for. Ephraim is the reference I have for this or rather, I should say my interpretation. There is no possibility of error, misprint or mistranslation and Ephraim and Noone are both authorities on chemistry. Am I correct in my interpretation? Am I correct that the interpretation of the underlined paragraph is suitably applied? And is there any grounds for my concerns? I insist that this is not to be an argument about evidence superceding the text book because if it is, the Brussels authorities will have to be approached.

I am not in a position to speak about medical aspects of Cr VI. Please consult internet site, "National Library of Medicine Chromium Compounds H. S.D.E Database" 90 pages TOXNET DATA NETWORK.

The values of chemistry must be brought to bear on this project. The developer needs to be requested to show a chemistry spread - sheet showing the effect of incineration on the feedstock before the whole perspective and impact on the community can be properly understood. Otherwise we are in a dangerous information deficit scenario. The water decomposition detail outlined and chromate substitution for sulfates requires the non-incineration of paint and the control and abatement of any other source of Chromium emissions.

I have no competence on the subject of chemistry but as a lay man I have read up as best I could and now I have outlined my concerns. It is difficult to find people who will speak on the subject. This raises further concern about how such issues are spotted and highlighted .... It will be an interesting subject for future historians.

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Dr Martin Hogan + Health Matters Institution Group  
Dr Martin Hogan on behalf of Inover at Bord Pleanála Oral  
Hearing 1<sup>st</sup> - 4<sup>th</sup> Oct 2012

**Dr Martin Hogan FRCPI FRCM AFOM**  
**Occupational Physician**  
**Specialist Registration No. 11908**

Employment Health Advisers Ltd., Heritage Business Park,  
Mahon Industrial Estate, Blackrock, Cork.

**Private & Confidential**  
Mr David McDermott,  
WYG Environmental and Planning Ireland Ltd,  
Nutigrove Office Park,  
Nutigrove Avenue,  
Rathfarnham,  
Dublin 14

23<sup>rd</sup> August, 2012

**RE: Indaver Ireland Waste to Energy Plant,  
Carranstown, Duleek, Co. Meath**

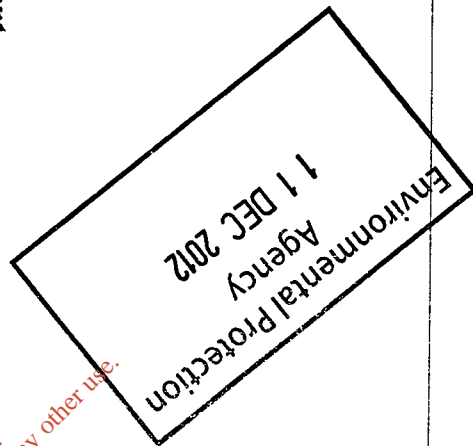
Dear David,

Thank you for asking me to comment on the proposed change of use for the above facility. As you know, I was involved in the original application to An Bord Pleanála and I researched and wrote much of the human health section of the original EIS. I also gave evidence on human health to the An Bord Pleanála oral hearing. As part of the development of this application WYG consulted with me and provided information relating to the proposed amendments to the facility and most importantly the emissions from the facility.

I understand the new application is for a 10% or 20,000 tonnes increase in annual maximum waste accepted at the facility and the inclusion of additional EWC codes which includes suitable hazardous and non-hazardous waste. It also included extension of waste acceptance and dispatch hours and additional ammonia and fuel oil storage tanks, an additional effluent treatment and engineering percolation area and conversion of the temporary to permanent status of two structures.

In the original application, there had been a number of concerns expressed in the submissions to An Bord Pleanála and subsequently at the oral hearing with regard to concerns with regard to emissions from the then proposed facility. Some of these appear to be restated now.

I understand the facility has now been in operation for a number of months. I also understand from information provided by Indaver Ireland and WYG that emission levels have been well below permitted emissions as set out in the facility licence and



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indeed at times, items such as dioxins have been below detectable levels. This is very much as had been predicted by the operators of the facility but had been doubted by some individuals and groups.

I see that the new application involves additional waste acceptance. I do also note that one of the issues was that the current waste being taken has a lower thermal value than was expected. I understand this may be due to the fact that there was a lower calorific value in the waste perhaps due to a higher than expected amount of putrescible waste.


I do note that the actual incineration process and flue cleaning and energy recovering system will remain unchanged from those as built under the existing planning permission and waste licence and I understand there is no material alteration to emissions to the atmosphere from the stack and there are no increases or changes to emission limit values for stack emissions. This is confirmed in the Air Quality chapter of the EIS accompanying the current application.

I was asked to comment on the potential health effects of the additional capacity. In human health terms and environmental terms, it is not what goes into a plant which matters but rather what comes out or the emissions. I note that the emissions are well below permitted levels. It previously was assessed that even if emissions were up to permitted levels no environmental human health effects would be expected. The fact the actual emissions from the facility have proved below those levels would in my mind reassure most individuals. While there may be some concern with the proposal to take in waste classified as hazardous, again in terms of human health impacts, it is any potential changes in emissions that might result that would be of significance and I do note that there is no expected change in emissions either being foreseen or allowed. In these circumstances there will be no human health effect from taking in this waste.

In these circumstances, I do not believe there is any likelihood of any significant impact on human health. I do not believe that in these circumstances it is necessary to revisit the assessment performed for the original EIS. I also do not believe there is any merit in considering baseline or other health assessments. These are notoriously difficult to organise and give very little usable information. I do not know of any location where they have been performed on similar sites where information has been gathered which has been of any practical uses.

In summary I do not envisage Human Health effects from the changes proposed in the application.

Yours Sincerely,

  
Dr Martin Hogan FRCP FRCPI FRCMI  
Consultant Occupational Physician (IMC No. 11908)

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**CHRISTY, HENRY** (1810-1865), English ethnologist, was born at Kingston-on-Thames on July 26, 1810. From 1850-58 he travelled in Europe and America, studying ethnology. In 1858 the discoveries by Boucher de Perthes of flint implements in France and England were first held to have proved the great antiquity of man. Christy joined the Geological Society, and with his friend Edouard Lartet explored the caves in the valley of the Vézère. An account of the explorations appeared in *Comptes rendus* (Feb. 29, 1864) and *Transactions of the Ethnological Society of London* (June 21, 1864). He died, on May 14, 1865, leaving a half-finished book, entitled *Reliquiæ Aquitanicæ*, which was issued in parts and completed first by Lartet and, after the latter's death in 1870, by Professor Rupert Jones. Christy left his magnificent archaeological collection to the nation. In 1884 it was placed in the British Museum.

**CHROMATES AND DICHROMATES**, inorganic chemical compounds, or salts, in which the element chromium appears as part of the acid or "negative" component of the salt. Chromium trioxide,  $\text{CrO}_3$ , commonly but incorrectly termed chromic acid, forms no crystalline hydrates with water, though its strongly acid aqueous solution is supposed to contain chromic acid,  $\text{H}_2\text{CrO}_4$ . The salts of this acid are known as chromates. Only normal salts, for example potassium chromate,  $\text{K}_2\text{CrO}_4$ , are known, which are analogous to and frequently isomorphous with normal sulphates. Acid or hydrogen salts, analogous to potassium bisulphate,  $\text{KHSO}_4$ , are unknown. If an equivalent of acid be added to a solution of a normal chromate, the colour changes from yellow to orange-red, and from the mixture dichromates, for example potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , alone can be isolated. If further equivalents of acid or, better, chromium trioxide, be added, the solutions become darker red and trichromates such as potassium trichromate,  $\text{K}_2\text{Cr}_3\text{O}_{10}$ , and tetrachromates such as potassium tetrachromate,  $\text{K}_2\text{Cr}_4\text{O}_{13}$ , are formed. The solid tri- and tetrachromates are decomposed on solution in water to form dichromates and free chromic acid.

Normal chromates are known of nearly all the stronger bases, both organic and inorganic, and are generally yellow. Ammonium, lithium, sodium, potassium, cuprous, cupric, rubidium, caesium, magnesium, calcium, zinc, cobalt and nickel chromates are soluble in water; strontium and the "rare-earth" chromates are sparingly soluble in water; mercuric chromate is decomposed by water, while silver, thallous, mercurous, cadmium, barium and lead chromates are insoluble in water. With the exception of cuprous, mercurous and magnesium dichromates which are unknown, all the metals forming soluble chromates also yield soluble red dichromates. Barium, lead and silver dichromates are known but are decomposed by water to form normal chromates and chromic acid.

chloride,  $\text{CrCl}_3$ , volatile liquid, chloride of chromium, unknown.

Though chromates are soluble in warm solutions, they form peroxide and form peroxide. It is accordingly in chromates being in the state of peroxidation formula  $\text{R}_3\text{CrO}_7$  hydrogen peroxide at low temperature and occasioning these peroxide is actant in the  $\text{H}_3\text{CrO}_8 \cdot 2\text{H}_2\text{O}$  hydrogen peroxide being solution. The blue color on neutralization have the general more oxygen with excess oxygen are obtained chromates are cyanide formula  $\text{CrO}_3$  regarded as a hydrogen peroxide molecule of peroxide yield hydrogen peroxide peroxide.

#### Analytica

tested by the chloride with

precipitated and mercurous chromates, chromates formation of chromate

TEXT BOOK OF INORGANIC CHEMISTRY

BY

DR FRITZ FERRARI

+ BY

DR P.C.C. THORNE (TRANSLATOR)

PRE WW II TEXT BOOK

METALLIC OXIDES—ACIDIC

CHAPTER XVI

*General methods of preparation—Stability—Manganates and permanganates—Ferrates, chromates, dichromates and polychromates—Halogen derivatives of chromic acid*

WHEN a metal has several oxides the basic properties of the hydroxides become less pronounced as the valency of the metal increases. Thus  $\text{Fe}(\text{OH})_3$  is a weaker base than  $\text{Fe}(\text{OH})_2$ , and  $\text{Sn}(\text{OH})_4$  is less basic than  $\text{Sn}(\text{OH})_2$ ; the decrease in basic power is shown by the greater hydrolysis of the salts of the higher hydroxide. When a certain limit in valency is reached the basic properties disappear almost completely and salt formation does not take place to an appreciable extent. The salts of  $\text{Mn}(\text{OH})_6$ , for example, hardly exist at all; and when oxides containing more oxygen than the neutral oxide are formed, they have definitely acidic properties. The oxides of hexa- and septavalent manganese give salts in which they function only as acid oxides. Another way of stating the result is to say that as the ionisation into OH ions becomes weaker, that into H ions increases. Further, if the metal is regarded as the positive part of the oxide and the oxygen as the negative part, the tendency of the oxide to approximate to the metal in its properties becomes less as the proportion of oxygen increases, and the compound thus becomes more electronegative. The higher oxides and chlorides of the metals are more volatile than the lower ones, as they tend to approach oxygen or chlorine in their behaviour.

Thus acidic oxides are formed only by those metals which can exert a high valency and thus combine with several oxygen atoms. The acidic tendency is sometimes shown even in the quadrivalent condition (Pb, Sn), but appears almost invariably in the quinquevalent and higher states of the metal. The metals in the right-hand half of the periodic table give the acidic oxides. The acids cannot always be isolated in the pure form, as they are frequently converted into the anhydride (chromic acid) or suffer extensive decomposition (ferric acid, manganic acid) or are polymerised (molybdic acid) when liberated from their salts.

The most important of these acids are: manganic, permanganic



and ferric acids; chromic, molybdic, tungstic and uranic acids; vanadic, niobic and tantallic acids. (The acids of the metalloids arsenic and antimony and of bismuth are discussed on pp. 626-630; those of the noble metals on p. 377.)

These acids show great variety in their properties; some are only known as salts and do not exist even in solution ( $H_2MnO_4$ ,  $H_2FeO_4$ ); others are known in concentrated solution, but decompose when an attempt is made to isolate them ( $HMnO_4$ ,  $H_2CrO_4$ ); others, again, exist in fairly concentrated pseudo-solution, but once isolated are only brought into solution again with great difficulty (molybdic, tungstic, uranic, vanadic, niobic and tantallic acids)—there is no reversible equilibrium in their solutions between the dissolved and the solid material. A similar set of differences exists in the salts of the acids; the acids of iron and manganese form only normal salts, chromic acid also forms salts in which a molecule of the anhydride is combined with the normal salt (anhydro-salts); while in the other acids of this class the effects of condensation and polymerisation are much more pronounced, and auto-complexes of high molecular weight and great stability are formed. This property is connected with that of forming heteropolyacids (cf. p. 405). It is obvious that comparisons between one group of these acids and another can seldom be drawn with advantage.

**Formation and Stability.**—The most important method of preparation is common to all these acids: the salts are obtained when a lower oxide of the metal is heated with alkali in the presence of an oxidising agent. When the acidic oxide is the most stable of the oxides of the metal it is formed when the metal itself or its lower oxides, hydroxides or sulphides are roasted in the air even when alkali is not present ( $MoO_3$ ,  $WO_3$ ,  $UO_3$ ,  $VO_3$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ). The oxides of Cr, Fe and Mn which are obtained in this way are not, however, the acidic oxides but lower oxides ( $Cr_2O_3$ ,  $Fe_2O_3$ ,  $Mn_2O_3$ ), and the higher oxides are formed only when alkali is present. The lower oxides can be fused with caustic potash or soda (or the carbonates) with admission of air, and the oxy-salts are formed, e.g.  $Cr_2O_3 + 2Na_2CO_3 + 3O = 2Na_2CrO_4 + 2CO_2$ . The probably with the alkali peroxide as an intermediate product. The oxidation is more rapidly and easily carried out if alkali nitrates or chlorates are used as oxidising agents instead of atmospheric oxygen, as they provide a more readily available supply of oxygen. It is remarkable that the oxidation of manganese to the manganate stage,  $K_2MnO_4$ , is incomplete; when a large excess of alkali is present a melt is obtained which contains only 2.6 atoms of oxygen per atom of manganese instead of the 3 atoms required by  $MnO_3$ . The mass has an intense dark green colour, and Sackur has shown<sup>1</sup> that it contains manganites, i.e. salts of the anhydride  $MnO_2$ , mixed with the manganate.

<sup>1</sup> *Ber.*, 1910, 43, 381, 448; 1911, 44, 777.

The potassium compound has the formula  $8K_2O$ ,  $Mn_2O_{13}$ , while that obtained from sodium salts is  $4Na_2O$ ,  $Mn_2O_6$ ; but it is more likely that solid solutions are formed, and not definite compounds, as there is no indication of an equilibrium between manganite and manganate—the same product is also obtained when potassium permanganate is heated alone or with alkalis. Baryta or lime can be used in place of caustic potash or soda. The formation of permanganate is interesting, for it is not a primary product of the oxidation of the lower oxides, but results from the decomposition and further oxidation of the manganate formed. When  $MnO_2$  is heated with alkali alone, manganate is produced at  $130^\circ$  by the decomposition  $3MnO_2 \rightarrow MnO_3 + Mn_2O_3$ , the  $MnO_3$  combining with the alkali. The  $Mn_2O_3$  is oxidised to  $MnO_2$  only at a red heat, when the above decomposition is repeated.

The manganate itself is also decomposed on further heating with formation of lower oxidation products and gives a definite dissociation pressure, which for  $K_2MnO_4$  is as follows:

Temperature . . . . .	$507^\circ$	$572^\circ$	$629^\circ$	$667^\circ$
Pressure of oxygen . . . . .	11	52.6	221	532 mm.

In a mixture of oxides of manganese and base, such as is obtained when permanganate is heated, the following apparently reversible dissociation pressures are obtained:

Temperature . . . . .	$505^\circ$	$560^\circ$	$600^\circ$
Pressure of oxygen . . . . .	50	129	400 mm.

Similar conditions obtain in the red melts formed by the fusion of iron compounds with alkali with access of air or addition of nitrate or chlorate. These contain ferrates, e.g.  $K_2FeO_4$ , but if formed at too high a temperature the ferrates, like the vanadates, are decomposed. When alkali vanadates are heated oxygen is given off with decrepitation, and if the residue is rapidly cooled a dark mass is obtained which contains vanadium in both the quadrivalent and quinquivalent states. On slow cooling, oxygen is absorbed and a clear red vanadate is obtained.

The normal chromates lose oxygen only at a high temperature, but the polychromates are more easily decomposed; thus, fused  $Na_2Cr_2O_7$  gives off oxygen at  $400^\circ$ . Even  $CrO_3$  is decomposed at high temperatures (p. 391). The salts of the other acids of this group (molybdic, tungstic, niobic and tantallic acids) can be fused without decomposition, or at least without loss of oxygen.

The above discussion indicates the best procedure in the preparation of these salts by the method of fusion with alkalis. When the anhydride of the acid is the commonest oxide of the metal (as with Mo, W, U, Nb, Ta, V) no oxidising agent need be added to the alkali. Niobates and tantalates are made in this way from the naturally occurring iron (manganese) niobate and tantalate (niobite, tantalite), and molybdates can similarly be made from lead molybdate (wulfenite), or from molybdenite  $MoS_2$  after roasting to  $MoO_3$ . Vanadates are also prepared from the natural heavy metal

PLEASE TURN TO PAGE 386  
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PARAGRAPH

vanadates, and tungstates from wolfram ( $\text{Fe, Mn})\text{WO}_4$  by roasting it in a furnace to render the iron insoluble and then fusing with sodium carbonate and leaching out the soluble sodium tungstate produced. In the manufacture of sodium uranate from pitchblende, as that salt is insoluble in water it is converted into soluble sodium uranyl carbonate by addition of sodium bicarbonate, and then precipitated as sodium uranate by addition of sulphuric acid. Oxidising alkali fusions are necessary for the production of the salts of chromium, iron and manganese, since only the lower oxides of these metals are found in nature. Pyrolusite is used as the raw material for the manufacture of manganates, and chrome ironstone, ferrous chromite,  $\text{Fe}(\text{CrO}_2)_2$ , for chromates.

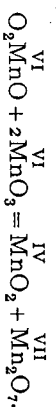
Only in a few instances can the acids be obtained directly by treatment of the ores with acids; but tungstic acid is formed when scheelite,  $\text{CaWO}_4$ , is treated with sulphuric acid, and niobic and tantalic acids can be prepared by fusing the minerals with potassium bisulphate. The acids remain as an insoluble residue contaminated with other substances, especially  $\text{TiO}_2$ , from which they can only be separated by conversion into the fluoro-salts (p. 292) and recrystallisation.

The method of oxidation in solution is sometimes employed for the preparation of these salts, but only for those made from lower oxides of the metal—iron, chromium and manganese. The reaction occurs more readily in alkaline solution, and ferric acid is not produced at all in acid solution as the free acid is unstable. Manganous and chromic compounds are oxidised by lead peroxide in nitric acid solution, a reaction which serves to detect minute quantities of manganese by the violet colour of the permanganic acid formed. Only chromium is oxidised by hydrogen peroxide and persulphates in acid solution, for permanganates are decomposed by excess of  $\text{H}_2\text{O}_2$ , thus providing a useful method of separating the two metals. In sulphuric acid solution the manganese is oxidised to the quadrivalent stage. Chromic salts are oxidised to chromates by permanganates.

In alkaline solution a great variety of oxidising agents can be used: hydrogen peroxide, persulphates, oxides of noble metals, hypochlorites, hypobromites, and other substances convert chromium salts into chromates, and similarly, but less easily, oxidise iron and manganese salts. Electrolytic oxidation is also frequently applied in alkaline solution for all three metals; an alkaline solution of the metallic salt or a suspension of the hydroxide in alkali is rapidly oxidised at the anode (which should be made of the same metal). Chromic salts are oxidised to chromic acid at the anode even in dilute sulphuric acid solution, and this method is used for the regeneration of the chrome liquors which are obtained when chromic acid is used on the large scale as an oxidising agent for organic substances. Permanganates and chromates are now usually manufactured by the electrolytic process, and even insoluble chromates like lead chromate (important as the pigment chrome yellow) can be made in this way; the solution of chromate or of chromic salt is electrolysed with a lead anode, and the lead chromate formed at the anode does not adhere if a little chlorate is added to the liquor. If no chlorate is added the anode

becomes coated with the insoluble chromate and the action stops, but the liberation of some chlorate ions prevents the formation of a continuous layer of chromate and thus exposes part of the anode to attack by the  $\text{CrO}_4$  ions.

**The Manganates and Permanganates.**—Manganic acid is probably a weak acid, while permanganic acid is a strong acid. *Manganic acid*,  $\text{H}_2\text{MnO}_4$ , is only known in the form of its salts and cannot be obtained in the pure state or even in aqueous solution; the anhydride  $\text{MnO}_3$  is equally unstable. *Permanganic acid*,  $\text{HMnO}_4$ , although unknown in the pure state, can be obtained in aqueous solution or as the anhydride  $\text{Mn}_2\text{O}_7$ . When an attempt is made to isolate manganic acid from solutions of its salts the acid decomposes into higher and lower oxidation products, thus:



Hence a precipitate of manganese dioxide separates out and the liquid becomes violet in colour owing to the permanganic acid formed. The latter can be reconverted into the green manganate by the addition of alkali, and on acidifying, the violet permanganate and the black precipitate are again produced. Even carbon dioxide suffices to set free the manganic acid from the manganate, and the  $\text{CO}_2$  normally present in the air is used technically to cause the transformation by blowing air through the solution from the green melt of manganate. Other acids, both strong and weak, act in the same way provided the acid has no reducing properties, e.g. hydrochloric acid cannot be used as it is oxidised to chlorine.

A solution of permanganic acid free from salts can be obtained by decomposing barium permanganate with the calculated quantity of sulphuric acid. It can be concentrated to contain 20 per cent.  $\text{HMnO}_4$ , but beyond that stage begins to give off oxygen. The concentrated solution decomposes readily into the *anhydride*  $\text{Mn}_2\text{O}_7$  and water, and as the oxide is somewhat volatile it can be recovered from the solution; it is most easily made by dissolving potassium permanganate in fairly concentrated sulphuric acid and warming to  $60^\circ$ . When the salt is added to the cooled concentrated acid, the oxide separates in oily drops—some dissolves in the acid to a green solution, and the rest forms a metallic-looking liquid below the acid. It is explosive, but not excessively so; it can be distilled on warming, giving a violet vapour, and sometimes detonates at a moderate temperature or when it comes into contact with oxidisable substances. Organic compounds are inflamed by it, and a black smoke of  $\text{MnO}_2$  is produced; in moist air the  $\text{Mn}_2\text{O}_7$  is slowly decomposed, the resulting oxygen being largely ozonised. The solution of  $\text{Mn}_2\text{O}_7$  in concentrated sulphuric acid is green, but on dissolving it in water the violet colour of permanganic acid is at once evident.



The solid manganates are not green like their aqueous solutions and melts; the potassium salt  $K_2MnO_4$  is pale brown to copper colour, while the sodium salt is black. The permanganates have a metallic lustre which can also be observed in the anhydride  $Mn_2O_7$ ; in fact, this bronze lustre seems to be peculiar to the higher manganese compounds, though some dyes, like rosaniline, show the same effect. In solution, the brown colour is lost and only the well-known violet persists.

Sodium and potassium manganates are very soluble, but the latter is less soluble when quantities of potassium hydroxide are present. The solubilities are fairly independent of temperature, and the salt must be crystallised from dilute potassium hydroxide. So far no manganates other than those of sodium and potassium have been obtained in the pure state. Of the permanganates, the potassium salt is the best known, as it can be obtained in stable crystals, whereas the sodium salt is deliquescent. It is not very soluble in cold water; 100 gm. of water dissolves:

Temperature.	-0.58°	+4°	10°	20°	40°	60°	75°
$KMnO_4$	3.0	3.4	4.4	6.5	12.5	22.0	32.4 gm.

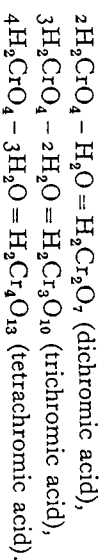
The solubility diminishes as the atomic volume of the alkali metal increases; thus at 60° the solubility of  $RbMnO_4$  is only 4.68 gm., and that of  $CsMnO_4$  1.25 gm. This relation has been noted in the perchlorates (p. 314), which the permanganates resemble in other ways; thus the salts of the alkaline earth metals and of the heavy metals of both classes are very soluble, and are also isomorphous, giving mixed crystals. On the other hand,  $NaMnO_4$  does not give mixed crystals with  $KMnO_4$ , nor does  $AgMnO_4$ . The manganates are likewise isomorphous with the chromates, sulphates and selenates of the same metals;  $K_2MnO_4$  is miscible with  $K_2SO_4$  and  $Na_2MnO_4$ ,  $10H_2O$  with the analogous Glauber salt  $Na_2SO_4 \cdot 10H_2O$ . The water of crystallisation in the two series is also the same—the potassium salts are anhydrous, while the sodium salts crystallise with 4, 6 and 10 mols. of water. The permanganates of the alkalis (except Li), of silver, univalent thallium and of barium are anhydrous; the other salts have water of crystallisation: the strontium salt, 4 mols., the calcium salt, 5 mols., the magnesium, zinc and nickel salts, 6 mols., the cadmium salt, 7 mols., and the copper salt, 8 mols. The solutions of the permanganates of the heavy metals decompose on prolonged boiling, and the ill-defined permanganates of aluminium, iron, etc., cannot be boiled at all without decomposition.

The permanganates are powerful oxidising agents in the solid state, and when alcohol is dropped on to solid calcium permanganate it is inflamed. This property persists in solution, especially when the permanganic acid is set free, as may be seen from the list on p. 115. Almost all substances with reducing tendencies show them in presence

of permanganate, which is reduced to the bivalent stage in acid solution and to the quadrivalent stage in alkaline or neutral solution, as the  $K_2O$  set free at once renders the neutral solution alkaline. With small quantities of such reducing agents as sulphites or alcohol, the reduction only proceeds as far as the manganate stage. Hydrogen sulphide, ferrous and stannous salts, halogen hydracids,  $H_2O_2$  and many other substances can reduce permanganate. Hydrogen reduces the salt at once when in the nascent condition, but only very slowly when in the molecular form. Oxalic acid is only reduced rapidly in the cold when a trace of a manganous salt is present; this gives  $MnO_2$  with the permanganate, which serves to reduce the oxalic acid, so that the reaction produces its own catalyst (autocatalysis).

**Ferrates.**—The ferrates are less stable than the manganates. They decompose even in alkaline solution with liberation of oxygen and separation of ferric hydroxide, but the reaction is diminished when the solution is cold and very strongly alkaline. These salts give dark amethyst to cherry red solutions, and the potassium salt,  $K_2FeO_4$ , can be obtained as a dark red powder from concentrated solutions containing much potassium hydroxide. The sodium salt is too soluble to be obtained in this way, but the difficultly soluble purple barium ferrate can be prepared by precipitating the solution of the potassium salt with a dilute solution of a barium salt. This compound is the most stable of the ferrates and can be dried at 100° without much decomposition. The ferrates are probably isomorphous with the manganates, chromates and sulphates.

**The Chromic Acids.**—The chromates correspond with the manganates in composition and method of formation (p. 380). They do not, however, show the same tendency to break up into compounds of higher and lower valency, and the hexavalent chromium is stable in both acid and alkaline solution. Indeed, the anhydride itself,  $CrO_3$ , can be obtained by acidifying concentrated chromate solutions, and there is no decomposition analogous to that of the manganates into permanganates and manganese dioxide. Chromium trioxide is deposited in deep red needles, on long standing, from a sulphuric acid solution of a chromate. It can be prepared alternatively by the decomposition of barium or lead chromates with the same acid and subsequent evaporation of the clear solution. No hydrates of this oxide in the colloidal state are known, and the slow formation of the crystals is characteristic, pointing to a slow condensation process of formation. Chromic acid indeed shows a marked tendency to form poly-acids by elimination of water, as in the following examples:





The trioxide probably has a still more highly polymerised molecule with a formula  $(\text{CrO}_3)_x$ . The change from  $\text{H}_2\text{CrO}_4$  to  $\text{H}_2\text{Cr}_2\text{O}_7$  is instantaneous, but the further polymerisations take a measurable time, at any rate when crystallisation ensues. The depolymerisation of  $\text{CrO}_3$  on solution in water is, however, very rapid.

The colour of chromium trioxide also indicates that it is highly polymerised, for it is redder than the di- or trichromates and is only approached in colour by the tetrachromates. The streak of  $\text{CrO}_3$  is darker than that of the tetrachromates. It appears to be depolymerised on heating, for it is partly volatile as a red vapour at  $200^\circ$  and thus resembles other oxides rich in oxygen (*e.g.*  $\text{OsO}_4$ ,  $\text{Mn}_2\text{O}_7$ ). A good deal decomposes before the temperature of volatilisation is reached, with formation of chromic chromate (p. 391) which is black, and final decomposition to the green,  $\text{Cr}_2\text{O}_3$ . Chromic anhydride is naturally a powerful oxidising agent and oxidises potassium, sodium, sulphur and phosphorus with the greatest ease. Hydrogen itself, ammonia, and hydrogen sulphide are oxidised when in the gaseous state; organic bodies (*e.g.* alcohol) are inflamed, and even paper is set on fire if some of the compound is left on it. The oxide is very hygroscopic and readily soluble in water. 100 g. water dissolve 164 g.  $\text{CrO}_3$  at  $0^\circ$  and 207 gm. at  $100^\circ$ .

When dilute solutions of chromates are acidified the acid is not precipitated like molybdic, tungstic and vanadic acids. On evaporating the solution no acid salts are obtained, but only the polychromates formed from the acid salts by loss of water:  $2\text{KHCrO}_4 \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$ . This reaction takes place spontaneously, and it may be supposed that there are many  $\text{HCrO}_4^-$  ions in the solution, for it becomes redder on acidifying, indicating the formation of ions of a different structure. Both the chromate ion  $\text{CrO}_4^{2-}$  and the solid chromates of formula  $\text{M}_2\text{CrO}_4$  are yellow, but on acidifying, the solutions pass through orange to red. The red colour of the dichromates of formula  $\text{M}_2\text{Cr}_2\text{O}_7$  is quite familiar, and the higher chromates are redder still in the solid state. It is thus likely that the various chromate ions,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Cr}_3\text{O}_{10}^{6-}$  and  $\text{Cr}_4\text{O}_{13}^{4-}$ , exist together in equilibrium in solution. There is not much evidence for the existence of the tri- and tetrachromate ions in dilute solution; for addition of water probably occurs,  $\text{H}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{CrO}_4$ , resulting in the ionic change  $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{HCrO}_4^-$ , and this change is more marked in the tri- and tetrachromates, which give dichromates on addition of water. These processes are instantaneous, as can be observed from the absorption spectrum, which does not follow Beer's law—a well-known generalisation which states that the absorption spectrum of a substance is independent of the dilution, and that the same quantity gives the same total absorption in dilute or concentrated solution. Hence when the absorption alters on dilution of a solution it follows that a change in

constitution has taken place: the mere increase in ionisation does not cause the alteration in the spectrum (cf. Hantzsch, p. 294). In the chromates the deviation from Beer's law is most simply explained as due to a greater complexity in concentrated solutions. Further, the conductivity of chromic acid increases with dilution to  $N/125$ , but after that diminishes; while that of potassium dichromate is also abnormal, for it first increases with dilution very slowly, and then much more rapidly after a certain dilution is attained. The first slow increase is explained by the hydrolysis  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HCrO}_4^-$ , as the  $\text{HCrO}_4^-$  ions are not very mobile. On further dilution the slow-moving  $\text{HCrO}_4^-$  ions are converted into the  $\text{CrO}_4^{2-}$  ions, which move more rapidly. Both  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$  are strong acids, but they only ionise readily to the monobasic stage, giving one H ion and  $\text{HCrO}_4^-$  and  $\text{HCr}_2\text{O}_7^-$ . Dichromic acid is somewhat stronger than monochromic acid. The dissociation of the second hydrogen atom—as often happens with strong polybasic acids—only occurs at great dilution, and here more readily in dichromic acid. In strong dibasic acids, one of the hydrogen atoms ionises almost completely before the dissociation of the second begins; it has been suggested that the first unit charge of electricity repels the approach of a second. The greater the amount of space between the positions occupied by the two charges, the smaller the opposing force; and since in the molecule  $\text{HO}\cdot\text{CrO}_2\cdot\text{O}\cdot\text{CrO}_2\cdot\text{OH}$  the hydrogen atoms are more remote from each other than in the molecule  $\text{HO}\cdot\text{CrO}_2\cdot\text{OH}$ , the entrance of a second charge in the former is attended with less difficulty.

The relative quantities of chromate and dichromate ions in solution have been determined in many ways. As the hydrolysis of the dichromate to the monochromate ion involves an increase in the number of dissolved molecules, the osmotic pressure, freezing point and boiling point methods are suitable for ascertaining the extent of this hydrolysis. Thus from the equation  $\text{H}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{CrO}_4$  a constant  $K = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{HCrO}_4^-]^2}$  is found. There are many other methods, *e.g.* that of Sherrill.<sup>1</sup> In solutions of both chromates and dichromates, however, equilibria are set up under the influence of the water, which tend to produce normal hydrolysis. The alkali chromates react alkaline, for the  $\text{CrO}_4^{2-}$  ions which are present have a strong tendency to become  $\text{HCrO}_4^-$  ions, according to the equation  $\text{CrO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCrO}_4^- + \text{OH}^-$ , thus liberating  $\text{OH}^-$  ions. Temperature has not much effect upon these equilibria.

**Salts of Chromic Acid.**—Most of the normal chromates,  $\text{M}_2\text{CrO}_4$ , are soluble in water or dilute acids. The yellow chromates of barium, lead and univalent thallium, and the dark red salts of silver, of univalent mercury and of bismuth are only slightly soluble. The

<sup>1</sup> *J. Amer. Chem. Soc.*, 1907, 29, 1641.



chromates and dichromates of a series of cobaltamines and chromium-ammines are also soluble with difficulty, e.g.  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{CrO}_4$ ,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cr}_2\text{O}_7$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{CrO}_4$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cr}_2\text{O}_7$ , and many others. The chromates of these metal amines may be precipitated and recrystallised from dilute acid solution, whereas di- or even higher chromates of the heavy metals are only obtainable from very concentrated solutions. Hence solutions of dichromates, which always contain some  $\text{CrO}_4^{2-}$  ions, give precipitates of the normal chromates with dilute barium, silver and similar salts. Dichromates of these metals do indeed exist, but can only be produced from acid solutions, which contain scarcely any  $\text{CrO}_4^{2-}$  ions.  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , for example, is produced from  $\text{Ag}_2\text{CrO}_4$  by the action of nitric acid of, at least, 0.075N strength, and is converted back to the monochromate by dilution. A more dilute acid is required to produce  $\text{BaCrO}_4$  by this method. Strontium chromate, which can be partially precipitated very readily even from neutral solution, at once dissolves in weak acids like acetic acid. On the other hand, the lead salt is hardly soluble in the most concentrated acids, so that the particular chromate obtained by precipitation depends only on the quantities used. These crystalline polychromates (recognisable by their red colour) may be converted into the yellow monochromates by simple treatment with more water. Polychromates of thallium are also easily prepared. The acid salts proper, having the formula  $\text{MHCrO}_4$ , are unstable and at once give dichromates, two molecules losing one molecule of water.

The different colours of the various monochromates are striking; whilst the majority are coloured yellow, irrespective of solubility, a few of the insoluble ones, such as the silver, mercury and bismuth salts, have an intense purple colour. This points to a difference of structure, for these metallic ions are themselves colourless. There are thus two types: the yellow or normal salts and the purple or pseudo-salts. The red chromates are used as indicators. For example, silver chloride (or cyanide) is less soluble than the chromate, so that if the latter is mixed with an excess of chloride solution, the deeply coloured silver chromate shows up, surrounded by the white chloride. It is possible in titrating a soluble chloride with silver nitrate to determine when all the  $\text{Cl}^-$  ions have been removed from solution, for at this stage any further addition of silver at once produces the brownish-red tint of the chromate. The coloration vanishes on adding a drop of chloride solution, as the insoluble red chromate is thereby converted into the soluble, pale alkali chromate:  $\text{Ag}_2\text{CrO}_4 + 2\text{NaCl} = 2\text{AgCl} + \text{Na}_2\text{CrO}_4$ . The well-characterised basic salts of chromic acid are also yellow, the best known of them being the easily soluble sodium salt,  $\text{Na}_4\text{CrO}_5 \cdot 10\text{H}_2\text{O}$ , of a sulphur-yellow colour, and the slightly soluble, bright yellow, bulky calcium salt,  $\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$ . The colours of the basic lead chromates are also interesting. If pre-

cipitated yellow lead chromate is treated with caustic soda, a scarlet mass is obtained, having one of the following formulae:  $2\text{PbO} \cdot \text{CrO}_3$ ,  $3\text{PbO} \cdot \text{CrO}_3$  or  $4\text{PbO} \cdot \text{CrO}_3$ . The difference in colour between mono- and dichromates is much greater than that between di- and tri-chromates, or even between di- and tetrachromates. The colour of chromates, despite its lightness, is very intense, so that mere traces of chromates are able to impart their colour to a solution. The same applies to the dark orange tint of the dichromates.

Of the alkali chromates, those of potassium, rubidium and caesium are notable for the ease with which they crystallise. The normal salts of these metals dissolve more readily than the acid salts, the reverse being true of the sodium salts. The sodium chromate crystals also contain water, the others yield anhydrous crystals. The caesium salts are the least soluble. The following figures give the solubility per 100 gm. water:

Temperature	0°	30°	60°	105.8°
$\text{K}_2\text{CrO}_4$	57.1	65.1	74.6	88 gm.
$\text{K}_2\text{Cr}_2\text{O}_7$	4.6	18.1	46.1	109 "
$\text{Rb}_2\text{CrO}_4$	38.3	44.1	48.8	" "
$\text{Rb}_2\text{Cr}_2\text{O}_7$	..	10.56	..	.. "

At 30°, 40.5 gm. of  $(\text{NH}_4)_2\text{CrO}_4$  and 47.2 gm. of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  dissolve in 100 gm. of water. All the foregoing salts are anhydrous. In contrast to these, the alkaline earth salts and the related lithium compounds contain water of crystallisation (the latter gives a monochromate with 0 and 2 mols. water, the bichromate with 2); the sodium compounds, of which the following are known, are also hydrated. The chromate with 0, 4, 6 and 10 mols.  $\text{H}_2\text{O}$ , the bichromate with 0 and 2; the tri-chromate with 0 and 2 mols. of water. The compound  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$  is analogous to Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . They are isomorphous with each other, yielding mixed crystals in all proportions. Its transition temperature, 19.525°, is so sharply defined that the solidifying of the melted salt in its own water of crystallisation may serve as a fixed point in thermometry. By fusion of the decahydrate, an unstable hexahydrate is produced, and can be detected up to 25.9°, this passing into a stable tetrahydrate which loses the rest of its water at 62.8°. The following points on the solubility curve have been chosen to illustrate these changes:

Temperature	0°	19.52°	25.9°	62.8°	80°	100°
Gm. anhyd. $\text{Na}_2\text{CrO}_4$ in 100 gm. water.	31.7	79.2	86.1	123.3	124.3	126.0

The solubility gradient of the anhydrous salt (i.e. above 62.8°) is thus very slight. The dihydrate of  $\text{Na}_2\text{Cr}_2\text{O}_7$  becomes anhydrous at 83°; its solubility is as follows:

Temperature	0°	52°	83°	93°	
Gm. $\text{Na}_2\text{Cr}_2\text{O}_7$	..	163.0	233.2	417	433

The tetrachromate  $\text{Na}_2\text{Cr}_4\text{O}_{13}$  has a solubility of 269.9 gm. at 0°.

In the alkaline earth chromates the power of combination with water and the solubility both increase in passing from barium to magnesium. While the barium salt is anhydrous and only slightly soluble (2.04 mg. in a litre of water at 0.88°, and 4.36 mg. at 28.08°), the magnesium salt is very soluble, and hydrates containing 5 and 7 mols. water are known. The solubility of calcium chromate is interesting: there are the anhydrous salt, and hydrates containing  $\frac{1}{2}$  and 1 mol.  $\text{H}_2\text{O}$



respectively, as well as two different ones with 2 mols.  $H_2O$ , and all these five calcium chromates have separate solubility curves. From the curves it is clear that the solubility of all these chromates *decreases* with increase of temperature, with the exception of one of the dihydrates of which more dissolves at higher temperatures. These relations are to some extent similar to those in the cerium sulphates (p. 736), and in general (cf. pp. 351, 478) calcium compounds are distinguished by their decrease in solubility with rising temperature. The appended table shows the percentage of anhydrous calcium chromate (using each hydrate) in saturated solution:

Mol. $H_2O$	0	$\frac{1}{2}$	1	2 (g)	2 (a)
At $0^\circ$	4.3	6.8	11.5	10.0	14.75
At $100^\circ$	0.42	0.8	3.1	(40°): 10.4	(45°): 12.53

Calcium forms acid salts up to tetrachromates; for basic salts see p. 388.

The acid chromates often form various modifications in the solid anhydrous state. Potassium dichromate is known to have this property and occurs in the form of thick, triclinic crystals, which melt at  $396^\circ$ ; large crystals separate from the fused mass on cooling, which are not identical with the original ones. They decompose on cooling, as they are unstable at a lower temperature, the purplish colour giving place to the orange red of the dichromate. This decomposition is reversible, the transition temperature being  $236^\circ$ . The rubidium compound  $Rb_2Cr_2O_7$  behaves very similarly and has three modifications. The ammonium compound gives no such change because, as described on p. 358, this salt evolves nitrogen when heated, leaving behind pure  $Cr_2O_3$ . The normal ammonium chromate  $(NH_4)_2CrO_4$  is not produced at high temperatures, and even at room temperature ammonia is lost, giving the stable red dichromate. On the other hand, various stable double salts of ammonium chromate are known, e.g.  $KNH_4CrO_4$ , and, like sulphuric acid, chromic acid has a tendency to form these alkali double salts, which are often very complicated. The formula  $K_3Na(CrO_4)_2$  serves to indicate the type of compound. The double compounds of the alkali chromates with halides of mercury are of special interest; their structure is still unknown. The formulae  $K_2CrO_4 \cdot 2HgCl_2$ ,  $K_2Cr_2O_7 \cdot HgCl_2$  and  $(NH_4)_2Cr_2O_7 \cdot 4HgCl_2$  may be quoted as examples; and it may also be mentioned that  $Hg(CN)_2$  gives similar compounds. These are somewhat similar to the double chlorides of mercury and the cobaltamine bases, e.g.  $[Co(NH_3)_6]Cl_2 \cdot HgCl_2$  or  $[Co(NH_3)_6]Cl_2 \cdot 3HgCl_2$ , etc.

Lead chromate or "chrome yellow" (cf. p. 382) can be precipitated equally well from chromates or dichromates. This compound is isomorphous with lead molybdate,  $PbMoO_4$ , and is the most insoluble of all the chromates, being also less soluble than most lead salts, except the sulphate. The fact that "chrome yellow" gradually assumes a red colour when exposed to air restricts its use as a paint, although the change can be retarded by mixing a little lead sulphate with it. Here it is not a question of a deepening in colour as a result of an increase in the size of the grains, as is perhaps the cause with  $HgO$  (p. 374),

because the initial product is distinctly crystalline; it is rather a definite transition to another form. Indeed, mercury and silver give red precipitates at once. For the behaviour of lead chromate towards alkalis see p. 389.

It does not seem possible to produce manganese chromate. When a manganese solution is added to a soluble chromate a precipitate is thrown down, but only very slowly, and its properties as a whole point to the manganese being in a higher state of oxidation than the bivalent stage. Consequently the valency of the chromium will be lower than 6, and oxidation and reduction have taken place at the same time.

A similar reaction occurs if a chromium salt is mixed with a chromate. It is possible that the substance produced is a chromate of chromium, e.g. the resulting brown residue may be accorded a formula  $2CrO_3 \cdot CrO_3$ ; alternatively, compounds of quadri- and quinquevalent chromium may be present. Compounds in which chromium is quinquevalent appear to exist, for if chromium trioxide acts in the cold upon very strong hydrochloric acid, a brown liquid results, from which double compounds of the types  $CrOCl_3 \cdot RCl$ ,  $CrOCl_3 \cdot 2RCl$  can be isolated, where R stands for potassium, rubidium, caesium, ammonium, pyridine or quinoline.<sup>1</sup> It is very likely that quinquevalent chromium really exists in these substances, as they form isomorphous mixtures with quinquevalent niobium. Hence the so-called "chromium chromate" probably represents an intermediate stage of oxidation. It is also obtained by heating  $CrO_3$  in dry air, oxygen being evolved; conversely by heating  $Cr(OH)_3$  in a stream of oxygen, or by heating chromium nitrate,  $Cr(NO_3)_3$  aq. These compounds, of which the brown  $2Cr_2O_3 \cdot CrO_3$  and the "chromium dioxide"  $CrO_2$  are the more remarkable, are all insoluble in water; the former is magnetic and the latter is black in colour. Other methods of preparing them are, in the wet way by precipitating chromates with a chromium salt, or by reducing the dichromate with nitric oxide, thiosulphate and other agents. The product obtained by these methods is gelatinous.

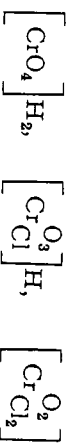
Oxidation reactions which are brought about by chromates and free chromic acid are fully described in different parts of this book. The oxidation potential is given on p. 115. Although these oxidations often proceed very quickly in acid solution, they go much more slowly in absence of acid. The speed of reaction can sometimes be observed, e.g. in the oxidation of hydrogen iodide, arsenious acid and of ferrous salts. Very often a catalytic agent is required to start the action, and ferrous ions,  $As_2O_3$ ,  $SO_2$ , compounds of quadri- and quinquevalent vanadium and others serve this purpose. It is believed, therefore, that the catalyst is at first oxidised to an unstable peroxide, which then in

<sup>1</sup> Meyer and Best, *Z. anorg. Chem.*, 1889, 22, 192; Weinand and Frieder, *Ber.*, 1906, 39, 4042.

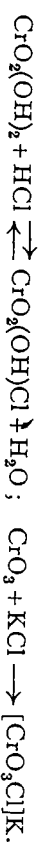
turn oxidises the "acceptor," that is, the hexavalent chromium is first of all reduced to the quinquivalent state, which exerts an oxidising effect, passing through the quadri- to the trivalent condition, the final product of the reaction.<sup>1</sup>

An obvious difference between chromic and permanganic acids lies in their behaviour towards hydrogen peroxide; whereas the latter undergoes reduction (p. 338), chromic acid can be oxidised to perchromic acid (see p. 419). Again, it is possible to obtain a chloride of chromic acid, chromyl chloride, from chromic and hydrochloric acids by removal of water before reduction of the  $\text{CrO}_3$  takes place, while the manganese acids only suffer reduction by hydrochloric acid.

**Chromyl Chloride, Chlorochromic Acid and related compounds.**—The oxygen atoms in chromic acid may be successively replaced by chlorine:



The displacement of one oxygen atom yields a monobasic acid, chlorochromic acid; and when both are replaced, a neutral body, chromyl chloride, is formed. Free chlorochromic acid is not known, but stable salts exist, produced from solutions containing chromic and hydrochloric acids and alkaline chloride; or alkaline chromate and hydrochloric acid give the salts on crystallisation



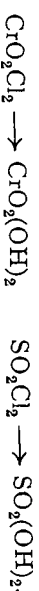
These compounds break down again if recrystallised from pure water, but can be obtained from solutions containing salt or acetic acid. They are well-defined reddish-yellow crystalline substances, and hold much water of crystallisation, in which they melt at a low temperature.

Analogous salts of a hypothetical fluorochromic acid, of a dark red colour, are also known. Bromo- and iodo-derivatives have also been described, but it is doubtful if they really exist, for it is likely that hexavalent chromium would be reduced by hydriodic acid, if not by hydrobromic acid as well.

The employment of larger quantities of HCl, in the presence of strong sulphuric acid (to absorb the water produced), drives the above reaction beyond the chlorochromate stage:  $\text{CrO}_2(\text{OH})_2 + 2\text{HCl} \rightleftharpoons \text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ . To prepare the chromyl chloride, a chromate is treated with alkaline chloride and strong sulphuric acid; the  $\text{CrO}_3$  and free HCl produced react with one another. Of course chromyl chloride may also be formed by the direct action of gaseous hydrochloric acid on chromium trioxide:  $\text{CrO}_3 + 2\text{HCl} \rightarrow \text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O}$ . Chromyl chloride exists as a dark reddish-brown liquid, very like bromine, and its vapour also resembles that of bromine. It has a density of about 2, boils at  $117^\circ$  and freezes at  $-96.5^\circ$ . It is soluble

<sup>1</sup> Luther and Rutter, *Z. anorg. Chem.*, 1907, 54, 1.

without decomposition in carbon tetrachloride, carbon disulphide, nitrobenzene, antimony pentachloride and similar liquids; it is, however, rapidly hydrolysed by water:  $\text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{CrO}_2(\text{OH})_2 + 2\text{HCl}$ . Thus chromyl chloride must be regarded as the acid chloride of chromic acid; the (OH) groups of the latter are replaced by chlorine. The substance belongs to the same class of compounds as sulphuryl chloride, the acid chloride of sulphuric acid:



Chromyl bromide and iodide appear to be just as incapable of existence as sulphuryl bromide and iodide. This property is made use of in the detection of chlorine in the presence of the other halogens. If a chloride is warmed with potassium dichromate and sulphuric acid, chromyl chloride distils over, and by absorption in alkali produces an alkali chromate. When bromine is present, however, no such volatile chromium compound is produced. The existence of chromyl fluoride is very provable. A blood-red liquid of large vapour pressure has been obtained from a mixture of chromates, fluorides and strong sulphuric acid, which has not so far been definitely analysed, but may be  $\text{CrF}_6$ .

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