

**THE PRINCIPLES OF
CHEMISTRY, PART
FOUR, PP. 276-499**

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The principles of chemistry, part four, pp. 276-499 by D. Mendeleeff

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BY
D. MENDELÉEFF

PART FOUR



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PRINCIPLES OF CHEMISTRY

(PART FOUR)

CHAPTER XXI

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, AND MANGANESE

SULPHUR, selenium, and tellurium belong to the uneven series of the sixth group. In the even series of this group there are known *chromium, molybdenum, tungsten, and uranium*; these give acid oxides of the type RO_3 , like SO_3 . Their acid properties are less sharply defined than those of sulphur, selenium, and tellurium, as is the case with all elements of the even series as compared with those of the uneven series in the same group. But still the oxides CrO_3 , MoO_3 , WO_3 , and even UO_3 , have clearly defined acid properties, and form salts of the composition MO_nRO_3 with bases MO . In the case of the heavy elements, and especially of uranium, the type of oxide, UO_3 , is less acid and more basic, because in the even series of oxides the element with the highest atomic weight always acquires a more and more pronounced basic character. Hence UO_3 shows the properties of a base, and gives salts UO_2X_2 . The basic properties of chromium, molybdenum, tungsten, and uranium are most clearly expressed in the lower oxides, which they all form. Thus chromic oxide, Cr_2O_3 , is as distinct a base as alumina, Al_2O_3 .

Of all these elements *chromium* is the most widely distributed and the most frequently used. It gives chromic anhydride, CrO_3 , and chromic oxide, Cr_2O_3 —two compounds whose relative amounts of oxygen stand in the ratio 2:1. Chromium is, although somewhat rarely, met with in nature as a compound of one or the other type. The red chromium ore of the Urals, lead chromate or crocoisite $PbCrO_4$, was the source in which chromium was discovered by Vauquelin, who gave it this name (from the Greek word signifying colour) owing to the brilliant colours of its compounds; the chromates (salts of chromic anhydride) are red and yellow, and the chromic salts (from Cr_2O_3) green and violet. The red lead chromate is, however, a rare chromium ore found only in the Urals and in a few other localities. Chromic oxide, Cr_2O_3 , is more frequently met with. In small quantities it forms the colouring matter of many minerals and rocks—for example,

of some serpentines. The commonest ore, and the chief source of the chromium compounds, is the *chrome iron ore* or chromite, which occurs in the Urals¹ and Asia Minor, California, Australia, and other localities. This is magnetic iron ore, $\text{FeO}, \text{Fe}_2\text{O}_3$, in which the ferric oxide is replaced by chromic oxide, its composition being $\text{FeO}, \text{Cr}_2\text{O}_3$. Chrome iron ore crystallises in octahedra of sp. gr. 4.4, it has a feeble metallic lustre, is of a greyish-black colour, and gives a brown powder. It is very feebly acted on by acids, but when fused with potassium acid sulphate it gives a soluble mass, which contains a chromic salt, besides potassium sulphate and ferrous sulphate. In practice the treatment of chrome iron ore is mainly carried on for the preparation of chromates, and not of chromic salts, and therefore we will trace the history of the element by beginning with chromic acid, and especially with the working up of the chrome iron ore into *potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$, as the most common salt of this acid. It must be remarked that chromic anhydride, CrO_3 , is only obtained in an anhydrous state, and is distinguished for its capacity for easily giving anhydro-salts with the alkalis, containing one, two, and even three equivalents of the anhydride to one equivalent of base. Thus among the potassium salts there is known the normal or yellow chromate, K_2CrO_4 , which corresponds to, and is perfectly isomorphous with, potassium sulphate, easily forms isomorphous mixtures with it, and is not therefore suitable for a process in which it is necessary to separate the salt from a mixture containing sulphates. As in the presence of a certain excess of acid, the dichromate, $\text{K}_2\text{Cr}_2\text{O}_7 = 2\text{K}_2\text{CrO}_4 + 2\text{HX} - 2\text{KX} - \text{H}_2\text{O}$, is easily formed from K_2CrO_4 , the object of the manufacturer is to produce such a dichromate, the more so as it contains a larger proportion of the elements of chromic acid than the normal salt. Finely-ground chrome iron ore, when heated with an alkali, absorbs oxygen almost as easily (Chapter III., Note 7) as a mixture of the oxides of manganese with an alkali. This absorption is due to the presence of chromic oxide, which is oxidised into the anhydride, and then combines with the alkali $\text{Cr}_2\text{O}_3 + \text{O}_2 = 2\text{CrO}_3$. As the oxidation and formation of the chromate proceeds, the mass turns *yellow*. The iron is also oxidised, but does not give ferric acid, because the capacity of the chromium for oxidation is incomparably greater than that of the iron.

A mixture of lime (sometimes with potash) and chrome iron ore is heated in a reverberatory furnace, with free access of air and at a

The working of the Ural chrome iron ore into chromium compounds has been firmly established in Russia, thanks to the endeavours of P. K. Ushakoff, who constructed large works for this purpose on the river Kama, near Elabong, where as much as 2,000 tons of ore are treated yearly, owing to which the importation of chromium preparations into Russia has ceased.

red heat for several hours, until the mass becomes yellow; it then contains normal calcium-chromate, CaCrO_4 , which is insoluble in water in the presence of an excess of lime.¹ ^{bis} The resultant mass is ground up, and treated with water and sulphuric acid. The excess of lime forms gypsum, and the soluble calcium dichromate, CaCr_2O_7 , together with a certain amount of iron, pass into solution. The solution is poured off, and chalk added to it; this precipitates the ferric oxide (the ferrous oxide is converted into ferric oxide in the furnace) and forms a fresh quantity of gypsum, while the chromic acid remains in solution—that is, it does not form the sparingly-soluble normal salt (1 part soluble in 240 parts of water). The solution then contains a fairly pure calcium dichromate, which by double decomposition gives other chromates; for example, with a solution of potassium sulphate it gives a precipitate of calcium sulphate and a solution of potassium dichromate, which crystallises when evaporated.²

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, easily crystallises from acid solutions in red, well-formed prismatic crystals, which fuse at a red heat and evolve oxygen at a very high temperature, leaving chromic oxide and the normal salt, which undergoes no further change: $2\text{K}_2\text{Cr}_2\text{O}_7 = 2\text{K}_2\text{CrO}_4 + \text{Cr}_2\text{O}_3 + \text{O}_2$. At the ordinary temperature 100 parts of water dissolve 10 parts of this salt, and the solubility increases as the temperature rises. It is most important to note that the dichromate does not contain water, it is $\text{K}_2\text{CrO}_4 + \text{CrO}_3$, the acid salt corresponding to potassium acid sulphate, KHSO_4 , does not exist. It does not even evolve heat when dissolving in water, but on the contrary produces cold, i.e. it does not form a very stable compound with water. The solution and the salt itself are poisonous, and act as powerful oxidising agents, which is the character of chromic acid in general. When heated with sulphur or organic substances, with sulphurous anhydride, hydrogen sulphide, &c., this salt is deoxidised, yielding chromic compounds.² ^{bis} Potassium dichromate³ is used in the arts and in chemistry as a source for the preparation of all other

¹ ^{bis} But the calcium chromate is soluble in water in the presence of an excess of chromic acid, as may be seen from the fact that a solution of chromic acid dissolves lime.

² There are many variations in the details of the manufacturing processes, and these must be looked for in works on technical chemistry. But we may add that the chromate may also be obtained by slightly roasting briquettes of a mixture of chrome iron and lime, and then leaving the resultant mass to the action of moist air (oxygen is absorbed, and the mass turns yellow).

³ ^{bis} The oxidising action of potassium dichromate on organic substances at the ordinary temperature is especially marked under the action of light. Thus it acts on gelatin, as Poutven discovered; this is applied to photography in the processes of photo-

chromium compounds. It is converted into yellow pigments by means of double decomposition with salts of lead, barium, and zinc. When solutions of the salts of these metals are mixed with potassium dichromate (in dyeing generally mixed with soda, in order to obtain normal salts), they are precipitated as insoluble normal salts; for example, $2\text{BaCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{BaCrO}_4 + 2\text{KCl} + 2\text{HCl}$. It follows from this that these salts are insoluble in dilute acids, but the precipitation is not complete (as it would be with the normal salt). The barium and zinc salts are of a lemon yellow colour; the lead salt has a still more intense colour passing into orange. Yellow cotton prints are dyed with this pigment. The silver salt, Ag_2CrO_4 , is of a bright red colour.

When potassium dichromate is mixed with potassium hydroxide gravure, photo-lithography, pigment printing, &c. Under the action of light this gelatin is oxidised, and the chromic anhydride deoxidised into chromic oxide, which unites with the gelatin and forms a compound insoluble in warm water, whilst where the light has not acted, the gelatin remains soluble, its properties being unaffected by the presence of chromic acid or potassium dichromate.

* Ammonium and sodium dichromates are now also prepared on a large scale. The sodium salts may be prepared in exactly the same manner as those of potassium. The normal salt combines with ten equivalents of water, like Glauber's salt, with which it is isomorphous. Its solution above 30° deposits the anhydrous salt. Sodium dichromate crystals contain $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. The ammonium salts of chromic acid are obtained by saturating the anhydride itself with ammonia. The dichromate is obtained by saturating one part of the anhydride with ammonia, and then adding a second part of anhydride and evaporating under the receiver of an air-pump. On ignition, the normal and acid salts leave chromic oxide. Potassium ammonium chromate, NH_4KCrO_4 , is obtained in yellow needles from a solution of potassium dichromate in aqueous ammonia; it not only loses ammonia and becomes converted into potassium dichromate when ignited, but also by degrees at the ordinary temperature. This shows the feeble energy of chromic acid, and its tendency to form stable dichromates. Magnesium chromate is soluble in water, as also is the strontium salt. The calcium salt is also somewhat soluble, but the barium salt is almost insoluble. The isomorphism with sulphuric acid is shown in the chromates by the fact that the magnesium and ammonium salts form double salts containing six equivalents of water, which are perfectly isomorphous with the corresponding sulphates. The magnesium salt crystallises in large crystals containing seven equivalents of water. The beryllium, cerium, and cobalt salts are insoluble in water. Chromic acid dissolves manganous carbonate, but on evaporation the solution deposits manganese dioxide, formed at the expense of the oxygen of the chromic acid. Chromic acid also oxidises ferrous oxide, and ferric oxide is soluble in chromic acid.

One of the chromates most used by the dyer is the insoluble yellow lead chromate, PbCrO_4 (Chapter XVIII., Note 46), which is precipitated on mixing solutions of PbX_2 with soluble chromates. It easily forms a basic salt, having the composition $\text{PbO} \cdot \text{PbCrO}_4$, as a crystalline powder, obtained by fusing the normal salt with nitre and then rapidly washing in water. The same substance is obtained, although impure and in small quantity, by treating lead chromate with neutral potassium chromate, especially on boiling the mixture; and this gives the possibility of attaining, by means of these materials, various tints of lead chromate, from yellow to red, passing through different orange shades. The decomposition which takes place (incompletely) in this case is as follows: $2\text{PbCrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 = \text{PbCrO}_4 \cdot \text{PbO} + \text{K}_2\text{Cr}_2\text{O}_7$ —that is, potassium dichromate is formed in solution.

or carbonate (carbonic anhydride being disengaged in the latter case) it forms the *normal* salt, K_2CrO_4 , known as *yellow chromate of potassium*. Its specific gravity is 2.7, being almost the same as that of the dichromate. It absorbs heat in dissolving; one part of the salt dissolves in 1.75 part of water at the ordinary temperature, forming a yellow solution. When mixed even with such feeble acids as acetic, and more especially with the ordinary acids, it gives the dichromate, and Graham obtained a trichromate, $K_2Cr_3O_{10} = K_2CrO_4 \cdot 2CrO_3$, by mixing a solution of the latter salt with an excess of nitric acid.

Chromic anhydride is obtained by preparing a saturated solution of potassium dichromate at the ordinary temperature, and pouring it in a thin stream into an equal volume of pure sulphuric acid.⁴ On mixing, the temperature naturally rises, when slowly cooled, the solution deposits chromic anhydride in needle-shaped crystals of a red colour sometimes several centimetres long. The crystals are freed from the mother liquor by placing them on a porous tile.^{4 bis} It is very important at this point to call attention to the fact that a hydrate of chromic anhydride is never obtained in the decomposition of chromic compounds,

⁴ The sulphuric acid should not contain any lower oxides of nitrogen, because they reduce chromic anhydride into chromic oxide. If a solution of a chromate be heated with an excess of acid—for instance, sulphuric or hydrochloric acid—oxygen or chlorine is evolved, and a solution of a chromic salt is formed. Hence, under these circumstances, chromic acid cannot be obtained from its salts. One of the first methods employed consisted in converting its salts into volatile *chromium hexafluoride*, CrF_6 . This compound, obtained by Unverdorben, may be prepared by mixing lead chromate with fluor spar in a dry state, and treating the mixture with fuming sulphuric acid in a platinum vessel: $PbCrO_4 + 3CaF_2 + 4H_2SO_4 = PbSO_4 + 3CaSO_4 + 4H_2O + CrF_6$. Fuming sulphuric acid is taken, and in considerable excess, because the chromium fluoride which is formed is very easily decomposed by water. It is volatile, and forms a very caustic, poisonous vapour, which condenses when cooled in a dry platinum vessel into a red, exceedingly volatile liquid, which fumes powerfully in air. The vapours of this substance when introduced into water are decomposed into hydrofluoric acid and chromic anhydride: $CrF_6 + 3H_2O = CrO_3 + 6HF$. If very little water be taken the hydrofluoric acid volatilises, and chromic anhydride separates directly in crystals. The chloranhydride of chromic acid, CrO_2Cl_2 (Note 5), is also decomposed in the same manner. A solution of chromic acid and a precipitate of barium sulphate are formed by treating the insoluble barium chromate with an equivalent quantity of sulphuric acid. If carefully evaporated, the solution yields crystals of chromic anhydride. Fritzsche gave a very convenient method of preparing chromic anhydride, based on the relation of chromic to sulphuric acid. At the ordinary temperature the strong acid dissolves both chromic anhydride and potassium chromate, but if a certain amount of water is added to the solution the chromic anhydride separates, and if the amount of water be increased the precipitated chromic anhydride is again dissolved. The chromic anhydride is almost all separated from the solution when it contains two equivalents of water to one equivalent of sulphuric acid. Many methods for the preparation of chromic anhydride are based on this fact.

^{4 bis} They cannot be filtered through paper or washed, because the chromic anhydride is reduced by the filter-paper, and is dissolved during the process of washing.