LXXV.—*On the Colour-properties and Relations of the Metals, Copper, Nickel, Cobalt, Iron, Manganese, and Chromium.*

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THE metals chromium, manganese, iron, cobalt, nickel, and copper form a group of elements with atomic weights progressing from 52.2 to 63.00, the mean lying somewhere between 57 and 58. They are characterised by salts corresponding to their normal oxides, which in dilute solution possess strongly developed and characteristic colours. The two lower members of the group belong to the even series in Mendelejeff's classification, the highest member, copper, to the odd elements, and the three intermediate members, iron, cobalt, and nickel, are part of the eighth series which links the odd and even elements together.

The partial investigation of the colour-properties of some of the elements of this group having revealed certain definite relations between them, it appeared probable that a comparative examination of the whole series might bring to light interesting and valuable information, and some experiments with iron, copper, and cobalt were instituted. Standard solutions were prepared containing 5 grams of each metal per litre; the copper and iron were weighed as metal, and the cobalt as sulphate after ignition to low redness. The iron was dissolved in dilute sulphuric acid, and oxidised with nitric acid, and the other solutions contained excess of both these acids. It became apparent on the first observation, that, on mixing the three solutions, a partial or total loss of colour resulted, and that at the same time the

liquid acquired the property of opacity, that is, of suppressing a certain portion of the white light passing through it.* On further trial it was found easy to mix the solutions so as to produce a neutral grey liquid. The proportions in which the metals must co-exist to give this optical neutrality were determined by trial in the following manner. A number of dry cylinders of white glass having been prepared, measured quantities of the standard solutions were placed in them in the proportions which seemed to give the nearest approach to an optically neutral liquid. The mixtures were then poured into tubes 20 centimeters long, closed at the ends by plates of glass. By looking through the columns and comparing the appearance with that presented by two partially crossed Nicol's prisms, situated at each end of a similar 20-centimeter tube, and by repeatedly making trial solutions, according as the result of the comparisons indicated, I found that perfect greyness is obtained by mixing 20 parts of the copper solution, 7 of the iron, and 6 of the cobalt. The solution so constituted appears in the 20-centimeter tube to be quite devoid of colour, but it suppresses a portion of the white light, and so causes the sky, or a white object viewed through it, to lose a portion of its brightness.

Cobalt, iron, and copper thus form a natural colour group, and their "colour-equivalents" are 20, 7, and 6 respectively, but these numbers must be considered to be tolerably close approximations only. The "colour-equivalents" are the numbers expressing the quantities of the metals required to produce an optically neutral mixture; the "colour-coefficients" are the reciprocals of the colour-equivalents, reduced to terms of the coefficient of copper as unity, and the colour coefficient of each element expresses the specific chromatic power of the element in the particular combination. For the present these terms must be taken to mean neither more nor less than this; but we shall find afterwards that it is possible to extend the definitions. The term "colour-coefficient" has already been used in this sense on discussing the colour relations of nickel and cobalt (*Proc Roy. I. A.*, 3, Ser. 2nd, Science); the colour-coefficient of iron, and possibly the coefficients of the other metals to a less extent, vary with the temperature; the determinations described above were made at about 18° C. The variation is insignificant for a few degrees, but if the neutral solution prepared at 18° be heated to boiling, the equilibrium is palpably disturbed, and the yellow colour of iron predominates. The colour-coefficient of iron also varies with the nature of the acid radical; the coefficient of iron dissolved in nitric acid is less than the coefficient of iron dissolved in sulphuric acid and oxidised with nitric acid.

* A brown mixture of iron, cobalt, and copper sulphate has been used by Vernon Harcourt as a standard in gas testing.

The relations of the solutions of the metals of this group are indicated in the accompanying diagram, where Cu, Fe, and Co are placed at the vertices of a triangle; any one of them is complementary to a definite mixture of the other two; iron is complementary to a mixture of cobalt and copper (violet), and cobalt to a mixture of iron and copper (green). A solution of a nickel salt is green, and by mixing iron and copper we can simulate the appearance of the nickel solution so closely, that the eye can detect no shade of difference. It is worthy of notice that the mean of the atomic weights of iron and copper, 59·5, is very near to the atomic weight of nickel. The mixture of iron and copper that most closely resembles nickel is not that which is complementary to cobalt. Such a solution contains an excess of iron, and therefore when mixed with cobalt, yields an opaque liquid, to which a decided yellow tinge is added. This is also what a mixture of cobalt and nickel in equivalent colour-proportions yields: therefore the analogy between the relations of the atomic weights of these elements and their chromatic relations is very close, for the atomic weight of nickel is sensibly lower than the mean of the atomic weights of iron and copper (59·5), that is, it approaches more nearly to the former than to the latter.

A copper solution is complementary to a mixture of iron and cobalt, and a copper solution is complementary to the reflection from the surface of copper; it follows then that the light transmitted by a mixture of iron and cobalt is similar to that reflected from copper. The truth of this assertion is apparent, as a dilute solution containing 7 parts of iron and 6 parts of cobalt has the peculiar red appearance characteristic of polished copper.

The chromatic properties of a metallic solution seem to be the result of several circumstances. The mean wave-length of the light absorbed by iron, nickel, cobalt, and copper increases as the atomic weight increases; the mean wave-lengths of the light absorbed by nickel and cobalt are nearly identical, because the light transmitted by cobalt contains the red and yellow, and the violet rays of the spectrum, and the light from nickel contains the rays composing the remainder of the spectrum, together with an excess of yellow rays common to both.

Speaking generally, we may say that the affinity of the metals of this group for oxygen increases with the colour-coefficients.

The colour-coefficients are in this order:—

Cu.	(Ni).	Fe.	Co.	Cr.Mn or Mn.Cr?
1	(1.05 about).	2.85	3.33	—

and this is the order which expresses the facility with which the oxides can be reduced by hydrogen, speaking roughly; it also expresses the electro-chemical order in which the metals follow each other when immersed in dilute nitric and sulphuric acids. This is Faraday's classification—copper, nickel, iron.

In speaking of the colour-properties of these metals I have in all instances referred to the salts corresponding to those oxides I have elsewhere (*Phil. Mag.*, Feb., 1879) distinguished as the normal oxides, in contradistinction to the protoxides on the one hand and the peroxides on the other. The solutions of the salts corresponding to the protoxides are usually either colourless or have an extremely faint colour.

Copper and chromium have colourless proto-salts, and the proto-salts of iron and manganese appear slightly coloured in concentrated solution. The proto-salts of manganese are sometimes said to be colourless, but I have always found them, when pure, to possess a faint rose tint resembling that of cobalt.* That this tint is not due to cobalt is evident from the fact that ammonium sulphide throws down an unsullied flesh-coloured precipitate from such solutions. It is not due to a trace of the higher salts, because treatment with reducing agents, for instance sulphurous acid, does not impair it.

It is not always easy to determine which is the normal oxide of a metal; reasoning, however, from analogy with iron, and from the reactions of the various oxides, we should be inclined to regard Mn_2O_3 as the normal oxide of manganese. This view is strengthened on consideration of the colour-properties of the metal, because the salts corresponding to MnO are colourless, or nearly so, as are the proto-salts of iron, copper, and chromium. On the other hand, the salts formed by dissolving Mn_2O_3 in cold hydrochloric or sulphuric acid are intensely coloured, resembling in this respect the salts of iron, cobalt,

* Statements regarding the colour of the proto-salts of manganese differ considerably.

nickel, copper, and chromium. Manganese in this form has a very high coefficient.

In describing the colour-properties of these elements I have always referred to dilute solutions. In dilute solutions the conditions are simplest, just as gases that obey Boyle and Mariotte's laws when remote from their condensing points fail to obey it when on the point of becoming liquids, so metallic salts in dilute solution and completely hydrated exhibit their characteristic colours, which sometimes become disturbed or undergo abrupt transitions when by concentration or increase of temperature the state of hydration of the salts becomes altered.

Solutions of chromium salts have a variety of colours; they may be green, blue, violet, or red, or of any intermediate tint. If to 10 c.c. of a solution containing 5 grams of chromium per litre, prepared by reducing potassium bichromate with sulphuric acid and alcohol, excess of caustic potash be added until the precipitate redissolves, a yellowish-green solution is obtained, and this reacidulated with sulphuric acid becomes bluish-green. If the 10 c.c. after treatment in this manner be added to 100 c.c. in a flask, a solution containing 0.5 gram of chromium per litre is obtained, and this solution when mixed with cobalt produces an optically neutral, but partially opaque, liquid. If 6 c.c. of cobalt (0.5 gram Co = 1 litre) be taken, about 25 c.c. of the chromium solution (0.5 gram Cr = 1 litre) will be required to produce optical neutrality, so that the colour-coefficient of chromium in this form is rather high.

The red salts of chromium may be prepared by the action of ammonia. This alkali, added in excess to a solution of chromium sulphate, precipitates a portion of the chromium as hydrate and retains the remainder in solution. The liquid filtered from the precipitate is reddish-purple, but becomes red on addition of sulphuric acid; a little sulphurous acid increases the purity of the tint. The sulphurous acid may afterwards be oxidised by nitric acid. The red salts of chromium so obtained strongly resemble dilute cobalt solutions, and like them are complementary to the green mixture of copper and iron (in equivalent colour-proportions) with which they form by admixture a grey liquid. Thus there seems to be in chromium salts a tendency to become identical in colour with the green mixture of 7 parts of iron and 20 parts of copper on the one side and with solutions of cobalt on the other. But it is possible to obtain chromium solutions of a different character. Moderate excess of ammonia added to a chromium sulphate solution dissolves, as we have seen, a portion of the precipitate forming the red solutions, but the chromium hydrate left undissolved is frequently of a blue colour, and gives when dissolved in sulphuric or nitric acid a blue solution. If instead of filtering the precipitate from

the ammoniacal liquid we reacidulate the whole with sulphuric or nitric acid, we obtain a violet solution approaching more nearly to pink, according as the solution is dilute and the amount of ammonia large, but possessing a full violet tint under some circumstances. These violet chromium solutions mixed with the green chromium solutions or with the green mixture of copper and iron in certain proportions, give blue chromium solutions. The red element in the violet solution is neutralised by the complementary green solution, a certain amount of opacity is conferred upon the liquid, and blue remains and is added to this. The blue solutions of chromium, as far as my experience enables me to judge, always have this characteristic. The amount of total absorption depends upon the quantities of the red and blue modifications that have neutralised, and the amount of blueness varies, being sometimes so small that the liquid has only a slate colour. The blue chromium salts appear to be identical in colour with the salts of copper, since a plate of copper viewed through them is perfectly white. It is easy to imitate the blue chromium salts by mixing copper solutions with the optically neutral liquid.

I have found it by no means easy to obtain the chromium salts in a state of perfect purity as regards colour; the red salts manifest on standing a tendency to become violet; the green salts are more easily obtained in a state approaching purity, but the solutions operated upon must be dilute. With manganese as with chromium, my experiments have hitherto been qualitative only; but they are sufficient to show that manganese forms modifications differing in their chromatic properties. These are obtained by dissolving the mixture of oxides prepared by the action of caustic alkali and alkaline hypochlorite on manganous salts. Under some circumstances, the manganese oxides catalyse the excess of hypochlorite; under other circumstances, the catalysis is arrested, and formation of permanganate of the alkaline base sets in. If the former condition of things is established and the precipitate is boiled for some time with the liquid, washed on a filter, and then dissolved in cold concentrated sulphuric acid, a pinkish-red solution, undistinguishable from a cobalt solution, is obtained. This solution is complementary to the green mixture of copper and iron, and gives by admixture with it a liquid, in most cases grey, but sometimes grey with a little tinge of yellow. These pink salts of manganese are permanent for some days in the cold, but the colour gradually fades, and is instantly destroyed by the introduction of caustic potash in quantity insufficient to neutralise the free sulphuric acid.

By dissolving the precipitated oxides of manganese in cold concentrated hydrochloric acid, brown solutions are produced, which, on dilution, become brownish-yellow. Manganese in this form is possibly analogous to the blue salts of chromium, inasmuch as they are opaque.

The brownish-yellow salts of manganese are exactly imitated by a mixture of iron and cobalt, with the optically neutral liquid. They are not, as far as I have seen, similar in colour to the mixture of iron and cobalt which is complementary to the salts of copper; they approach more nearly to iron. The following table exhibits the colour-properties of these elements, as studied up to the present; elements with solutions of similar colour are given in vertical lines:—

Yellow.	Orange.	Pinkish-red.	Violet.	Blue.	Green.
Fe Mn ?	(7Fe + 6Co) Copper reflection Mn (nearly)	Co Cr Mn	(20Cu + 6Co) Cr mixture	Cu Cr	20Cu + 7Fe Cr Ni (nearly)

These combinations give grey partially opaque liquids:—

Cobalt, iron, and copper.
 Copper solutions and copper reflection.
 Chromium (blue) and copper reflection.
 Copper, iron, and chromium (red).
 Copper, iron, and manganese (red).
 Chromium (green) and chromium (red).
 Chromium (green) and cobalt.

These grey liquids, excepting the first, I have not specially examined; the first has been submitted to a few experiments. It is within wide limits of the same neutral tint in all thicknesses, and the amount of light absorbed increases with the thickness of the liquid traversed.

This mixture will probably be found useful in the analysis of light from various sources; a candle flame seen through a column of it appears greenish-yellow, and a red-hot platinum wire appears of a bright lemon-yellow colour when viewed in the same manner. The solution retains its greyness when evaporated considerably; a special description of its properties will, I hope, form the subject of a future communication to the Society.

The accompanying diagram (p. 386) shows the absorption spectra of cobalt, copper, and iron. The solutions were of equivalent chromatic strength, so that equal volumes of the three mixed together formed a grey liquid.* Equal thicknesses of each were placed separately in front of the slit of the spectroscope, and the resulting spectra are shown in the diagram.

* The best method of observing all the conditions of the absorption of metallic solutions is that of Gladstone; but in comparing the effects of various metals the solutions should contain the metals in the proportions of their colour-equivalents.

The study of the absorption spectra of the various modifications of manganese and chromium confirms the results already described. The absorption spectra of the green salts of chromium are shown in the diagram; it will be seen that the spectrum is complementary to the cobalt spectrum; the solution was not quite pure (chromatically): hence the presence of the faint band of red. The red salts of chromium and of manganese give spectra containing the red and violet rays, and a dark band occupying the place of the dark band in the cobalt spectrum. The blue salts of chromium have an absorption spectrum resembling that of the copper salts. It is difficult to obtain the modifications of chromium and the red salts of manganese quite pure. The red salts of chromium, when not quite pure, have an excess of violet, probably because of the presence of the blue modification of chromium; the green salts often transmit the penetrating red rays referred to by Gladstone (*Chem. Soc. J.*, **10**, 79), and the optically neutral mixtures of the red and green sulphates of chromium, when the latter salts are not quite pure, reveal in the 20-centimeter tube the presence of these red rays, although without the assistance of the tube the liquid may seem perfectly devoid of colour. The red appearance of chromium salts in great thickness must not be confounded with the differentiation of the salts into the red and green varieties.

The red manganese salts, when not quite pure, seem to transmit a smaller proportion of violet rays than the cobalt salts. My observations indicate that the red salts of chromium and manganese tend to become identical in colour with cobalt as they progress towards purity.

We may divide the spectrum into three regions; (1) the red region, that covered by the absorption of copper; (2) the region covered by the absorption of cobalt, which we may call the green; and (3) the violet region, covered by the absorption of iron. It is possible that three modifications of chromium exist, each absorbing the rays contained in one of these three regions; the blue salts of chromium absorb the rays in the red region, and the red salts those in the green region; and there are possibly yellow salts capable of absorbing the rays of the violet region. The presence of such yellow salts in company with the blue and red salts would account for the suppression of white light effected by chromium salts. A green chromium solution, chromatically equivalent to a certain green mixture of iron and copper sulphates, is less transparent than the latter mixture is, and the same is true of the blue chromium salts.

In the same way it is possible there may be three modifications of manganese, the red salts, the yellow salts, the existence of which is indicated by the nature of the orange solutions of manganese, and unknown blue salts, which, existing only in combination, impart to manganese solutions the opacity they sometimes, if not always, possess.

DIAGRAM SHOWING THE COMPARATIVE EFFECTS OF METALLIC SOLUTIONS OF EQUIVALENT COLOUR STRENGTHS.

The following conclusions appear to be fairly deducible from the experiments described in this paper:—

There are intimate relations between the metals Cr, Mn, Fe, Ni, Co, and Cu.

Absorption and transmission of light by solutions of the salts of these metals take place in three definite regions of the spectrum; these regions are shown in the diagrams (b), (c), and (d).

Each of the metals Fe, Co, and Cu forms salts, corresponding to one oxide, which are *usually* of one distinctive colour, and absorb light in one of the three regions of the spectrum.

Nickel salts are *usually* green, and have two absorption bands.

Each of the two elements (with least atomic weight), viz., Cr and Mn, forms more than one kind of salt, each kind identical in colour-properties with the salts of one of the three elements Fe, Co, and Cu, or with a mixture of two of these elements of definite composition, and complementary in colour to the third.

In the case of Fe, Co, Ni, and Cu, the mean wave-length of the light absorbed is a function of the atomic weight.

In the case of the sulphates of the same four metals, the colour-coefficient or specific chromatic power of each element is independent of the atomic weight, and is greater than the colour-coefficient of any other of the four elements having a less affinity for oxygen, and less than the coefficient of any element with a greater affinity for oxygen.

The colour-coefficient varies, in some cases at least, with temperature, with the nature of the acid radical, and with the state of oxidation.