LI.—*On the Colour Properties and Colour Relations of the Metals
of the Iron-Copper Group.*

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A DILUTE solution of nickel sulphate is green, and can be exactly simulated by a mixture of iron and copper. When 7 parts of iron and 20 parts of copper are dissolved, as sulphates, in excess of a mixture of dilute sulphuric and nitric acids, a bluish-green solution is obtained, which is complementary to solutions of cobalt, and produces on admix-

ture, at 18°C ., with 6 parts of the latter metal dissolved as sulphate, a solution devoid of colour, but partially opaque.

This bluish-green mixture of copper and iron, compared with a solution of nickel sulphate, appears of a bluer tint, and a mixture of the sulphates of iron and copper, in order to simulate nickel sulphate, must contain a greater proportion of iron. The exact quantities required depend upon the temperature of the solution and upon the state of concentration. At 5° , in order to produce the tint of nickel solutions, about 1 part of copper and $1\frac{1}{2}$ parts of iron are required, if the solutions are dilute; but if this mixture be raised to 15° , and compared with dilute nickel sulphate at the same temperature, it is found to have become decidedly yellower, and now a mixture of equal parts of iron and copper is similar to the nickel solution.

But direct comparison of iron and copper mixtures with nickel solutions in this manner is inadequate to determine with the greatest accuracy the quantitative colour relations of the three metals, and I have therefore resorted to the method which has been already used successfully to determine the quantitative colour relations of iron, copper, and cobalt. For this purpose solutions were prepared as before, containing respectively 5 grams of each metal as sulphate. The solution of nickel was prepared by dissolving 13.163 grams of the sulphate, rendered anhydrous by ignition to low redness, in a considerable quantity of water, adding sulphuric acid and diluting to a litre.

A solution containing 20 parts of copper, 7 of iron, and 6 of cobalt, and chromatically neutral at a temperature of about 18° , being taken as the standard, the copper and nickel solutions were mixed in white glass cylinders, with 6 parts of cobalt at the same temperature, until after repeated trials a colourless mixture was obtained. This contained copper 13 parts, nickel 8.75 parts, and cobalt 6 parts, and was undistinguishable from the standard mixture. There are thus two colourless solutions containing the same quantity of cobalt, neutralised in the one case by 20 parts of copper and 7 of iron, and in the other by 13 parts of copper and 8.75 parts of nickel. As a consequence of this, 8.75 parts of nickel are equal, at any rate as regards quality of colour, to 7 parts of iron and 7 of copper. Considering only the three metals copper, nickel, and cobalt, their colour-equivalents are 13, 8.75, and 6 respectively, and their colour coefficients are (Cu) 1, (Ni) 1.48, (Co) 2.16. The colour coefficients of copper, iron, and cobalt, regarded as a neutral colour group, are (Cu) 1, (Fe) 2.85, (Co) 3.33; and since the quantities of cobalt involved in the two cases were identical, it is necessary to multiply the former series of coefficients by 1.54 to make the coefficients of cobalt equal in the two series, which are then capable of comparison—

Cu.	Ni.	Fe.	Co.
1	—	2·85	3·33
1·54	2·27	—	3·33

The coefficient thus obtained for nickel differs considerably from that suggested temporarily in my former paper (*viz.*, 1·05), which was obtained from the consideration of earlier experiments made in Prof. Galloway's laboratory in Dublin (*Proc. R. I. A.*, 2 ser., 3, Science), involving only nickel and cobalt, which do not in any proportions yield a colourless mixture, but it is interesting to observe how the relation between the sequence of the colour-equivalents and the manner in which the metals follow one another in affinity for oxygen and in electrochemical order still holds good. It is also worthy of notice that the coefficient of copper in the second series is increased by 0·54, while the coefficient of nickel is lower than the coefficient of iron by the same amount, and the sums of the two series are equal. This rise in the colour coefficient of copper is apparent and not absolute, because, as is seen by the foregoing experiments, and by the study of its absorption spectrum, the nickel causes absorption in two regions, the red and the violet, the former being the region absorbed by copper, and the latter by iron solution.

In this respect nickel differs from copper, iron, and cobalt, which in the state of sulphate of the oxides, and unassociated with other bases, have only one region of absorption, at least in the visible spectrum. Nickel thus, by virtue of its double absorption, simultaneously enacts the part of both iron and copper, for at 15—20° 8·75 parts of nickel replace 7 parts of iron in a grey mixture, and also reinforce the copper present, so that 13 and not 20 parts are required.

It must not be forgotten that chromium, manganese, and copper, and even nickel itself, are capable, in aqueous solution, of existence in more than one colour state, and of causing absorption or transmission in more than one of the three regions of the spectrum previously defined. Besides the blue salts of cupric oxide (CuO) and the colourless salts of cuprous oxide (Cu_2O), there are also, as is known, coloured salts of the latter. If to the deep blue solution of copper sulphate in ammonia a slight excess of strong sulphurous acid be added, the blueness is destroyed, and the liquid becomes sometimes colourless, but more often yellow. This colourless or yellow solution changes frequently almost instantaneously, at other times more slowly, into a deep copper-red liquid. The copper-redness of the liquid is caused by transmission in the "red region," and the solution consequently resembles in colour the reflection from metallic copper. Indeed the resemblance is perfect, and very striking under certain circumstances.

The copper-red solutions of copper are complementary to the blue

solutions; on dilution they become brownish-yellow, and finally colourless; mixed with potash and boiled, they deposit yellow cuprous oxide. During the process for determining carbon in iron by combustion, when the metallic copper deposited during digestion of the sample with copper sulphate is being dissolved in acidulated copper chloride, the red salts of copper usually manifest themselves, the opacity and approximate blackness of the liquid being due to admixture of the red salts with the excess of greenish-blue chloride of copper.

The blue solution of nickel sulphate in ammonia treated with sulphurous acid until the acid sometimes turns greenish-yellow, but often becomes pure yellow, and the latter solutions examined by the spectroscope show absorption in the violet region only, thus resembling iron salts. If cobalt sulphate be substituted for the nickel salt, a magnificent bright orange-coloured solution results. The nickel and cobalt solutions thus obtained by the use of sulphurous acid, on dilution or on standing, again become green and pink respectively.

The power of nickel to replace copper and iron remains when the nature of the light is changed. The solution of iron, copper, cobalt, which is colourless and opaque in diffused daylight, is dark green in gaslight, but a solution colourless and opaque in gaslight can be prepared, and has the composition iron 5, copper 20, cobalt 12 (or thereabouts, because no doubt the nature of gaslight varies). In daylight this solution appears pink. These equivalents were determined by comparing trial mixtures with distilled water, the water and the mixtures being contained in white glass cylinders, held a few inches above a white surface illuminated by the gas. A similar result is obtained by replacing the 5 parts of iron and 5 parts of the copper by 6.25 parts of nickel, for a solution containing nickel 6.25, copper 15, cobalt 12, was colourless in gaslight.

The grey solutions—and by this name are designated the mixtures of copper 20, cobalt 6, iron 7, and copper 13, cobalt 6, nickel 8.75—have some properties in common and some points of difference. They are both colourless at 15–20°, and at this temperature their absorption spectra are identical. The iron solution at lower temperatures is violet, and at higher temperatures greenish-yellow. At 5° the solution is perceptibly violet, at 30° perceptibly green, and at the boiling point strongly green. The grey nickel solution, on the other hand, does not vary perceptibly between the ordinary temperature and the boiling point. The grey iron solution, on concentration or in great thickness, preserves its main characteristics, but the coefficient of iron apparently diminishes slightly. The grey solution containing nickel varies less than the grey iron solution, and is scarcely affected by concentration to a considerable extent.

The white light absorbed by the grey solutions and the residual

white light transmitted are not ordinary white light. By reference to the accompanying diagram of the absorption-spectra of these solutions, the nature of the light is seen. The transmitted portion is compound white light, consisting of the rays of two complementary regions of the spectrum. Of the two transmitted bands, one has its centre in the yellow, and the other in the indigo. The diagrams represent the spectra obtained with a dense flint-glass prism. The yellow band in moderate thickness of the grey liquid consists of yellow fringed by red and green. As the thickness of the absorbent increases, the band dwindles until it consists only of yellow. The centre of this band is situated in the yellow part of the spectrum between D and E, but very near the former. The other band has its centre in the indigo between F and G, but nearer to the latter than to the former;* as the depth of the grey solution increases, the bands gradually disappear. The centres of the complementary transmitted bands are the boundary lines of the three regions that characterise the transmission and absorption-spectra of the aqueous solution of the metals of the group under consideration. For as the quantity of iron increases, the boundary of the dark band in the violet continues to approach the centre near G, and in the same manner the dark band of copper approaches the limit near D. The cobalt band has its limits in both centres. Of course the absorption-bands of the metals when in solution have not these limits; the absorption-band of iron, for instance, extends beyond the limit even in the diagram.

The nature of the light transmitted by the grey solutions accounts for the properties of these liquids. If the opacity and greyness were owing to a gradual suppression of all the rays in the spectrum in the proportions constituting ordinary white light, the colours of objects would be altered only in intensity and not in quality when seen through the solutions. As it is, the colours are extinguished altogether or considerably altered, when they are due to rays in the violet, green, or red regions of absorption, and altered very little, or not at all, when due to rays in the intermediate regions of transmission. A red-hot platinum wire appears lemon-yellow, because the red rays it contains are absorbed, and the yellow rays transmitted. The radiation from red-hot platinum contains only a small portion of the waves of higher refrangibility, and there is consequently a predominance of yellow light.

* The positions of the two complementary lines in the spectrum as fixed by these experiments agree with the position assigned to them by Prof. Grassmann, who says (*Phil. Mag.*, 1854) :—"The yellow lies between D and E of Fraunhofer, and about three times as far from E as from D, the indigo extends from the middle of the space between the lines F and G, almost to the line G, so that any indigo which lies between these limits furnishes white with any yellow which lies near the position already described.

Since the grey solutions owe their chromatic neutrality to the combination of the two complementary transmitted beams, and since these combine in definite proportions to produce white light, it follows that unless the composition of daylight is invariable, the solutions cannot always be colourless. The light of the sun is essentially yellow, a cloud illuminated by the direct solar ray is yellow compared with the cloud on a clear but not bright day, and the sun itself is yellower than the illuminated cloud. Ordinary diffused daylight in the morning differs from diffused daylight in the evening, when the beams pass more obliquely through the atmosphere. As the intensity of solar illumination increases, of course the rays of all refrangibilities increase, but the rays in the region of the yellow transmitted beam appear to increase more rapidly than the rays in the indigo region. For this reason the colour of the grey solutions is not invariable, and the term must be understood to refer to solutions grey under certain meteorological conditions. The grey solutions of the composition and at the temperatures defined, are colourless in clear diffused daylight at mid-day; in the evening they have a tendency to violet, and in bright sunlight they look yellowish-green. The sun itself looks yellower through the grey solutions than when observed directly. On a foggy day the solutions are distinctly greenish, and the coloration increases with the density of the fog. Probably the observation of a standard white surface through a long column of grey solution might be used to indicate the variations in the nature of daylight.

The grey solutions, prepared by substituting the red salts of manganese for the cobalt salts, have the same general properties as the other grey solutions, and their absorption-spectra have the two bright bands in the yellow and in the indigo. Grey solutions containing chromium, when concentrated or observed in great thickness are often found to be imperfect, and in many cases the conditions appear to be the negative of those which exist in the case of the other grey solutions, the band in the yellow and, less frequently, the band in the indigo, being darker than the remaining parts of the spectrum. The colour properties of chromium are complicated and obscure, and are worthy of further and attentive study. It is, as I have shown, possible to prepare colourless chromic salts, by mixing the complementary green and red salts, but besides these there are colourless chromic salts which are formed spontaneously. I obtained a solution of this kind by allowing a red chromic solution to stand for some months. The red solution was prepared by adding strong ammonia in excess to chromic acid, and acidulating the resulting clear solution with nitric acid. At first it was indistinguishable from a moderately dilute cobalt solution placed side by side with it in the window, and was of a full pink colour. After a time it faded and began to exhibit a yellowish tint,

and ultimately became colourless. When the colourless liquid was evaporated to dryness, and the residue ignited and fused with alkaline carbonate and nitrate, yellow alkaline chromate was formed.

An illuminated surface is extinguished when viewed through a sufficient thickness of the grey solutions, the thickness required corresponding to the degree of illumination of the surface. I hope to make use of this fact to determine the illumination of metallic surfaces in an investigation of the conditions of reflection from copper, the results of which I hope soon to have the honour of laying before the Society. The photometric measurements obtained in this way would have the advantage of being absolute, and therefore independent of any external and arbitrary standards.

The diagrams illustrating this paper show the effect upon the spectrum of increasing thickness of the solutions; the method employed was essentially the same as that used by Gladstone. The apparatus consists of a wooden box about two feet long and four inches deep, the box is blackened inside and closed at each end by wooden plates. The plate at the anterior end is furnished with a fixed narrow slit on the median vertical line, and at the posterior end a rectangular hole is cut just large enough to allow the insertion of the prism C, which is made capable of rotation about its axis. In front of

the slit is the hollow prism A, this in section is a square decimeter, but it is divided into two chambers as shown. The chamber next to the slit contains the metallic solution, and the anterior chamber is filled with distilled water. This arrangement ensures the passage through the slit of light from any object situated in the direction of the longer axis of the instrument. The eye placed at C observes the spectrum, in which are visible the most conspicuous lines of Fraunhofer, and when the prism is filled and placed in position the appearance indicated by one or other of the diagrams, according to the nature of the solution, is observed. The solutions were made of equivalent chromatic strength, the copper solution contained 50 grams of metal per litre. The first diagram shows the spectrum of the grey liquid containing 50 grams of copper and equivalent quantities of iron and cobalt per litre. It also shows the spectrum of the grey nickel solution containing the same quantity of cobalt per litre as was contained in the grey iron solution. Diagram No. 2 shows the absorption-spectrum of copper, No. 3 the absorption-spectrum of iron, No. 4 of cobalt, Nos. 5 and 6 illustrate the absorption-spectra of a nickel solution, and of a

copper-iron solution of equivalent chromatic strength. By using solutions of known strength, and a prism of constant dimensions, it is possible to put on record more definite information than when solutions of unknown strength and a prism of indeterminate dimensions are used ; and comparison with future experiments or with the work of other observers is made possible.

The black horizontal lines shown in the diagrams are obtained by

placing fine wire across the slit, at intervals of a centimeter; these horizontal lines and the lines of Fraunhofer subdivide the spectrum into rectangles, and so facilitate observation. These coloured solutions of equivalent chromatic strength do not appear equally coloured to the unaided eye, the iron solution seeming much less deeply coloured than the copper solution, and the copper solution than the cobalt solution, although each decomposes the same amount of white light.

This, I think, is because the rays absorbed by the iron solution, the violet rays, are less easily appreciated by the eye than the more easily appreciated red rays absorbed by copper, and the still more easily appreciated green rays absorbed by cobalt.

The experiments described in this paper point to the following conclusions:—

The colour effects of nickel in ordinary solutions can be produced by a mixture of copper and iron in varying and widely different circumstances.

A colourless opaque solution, resembling the colourless opaque iron-copper-cobalt solution, can be produced by mixing nickel, copper, and cobalt solutions.

These colourless opaque solutions in sufficient thickness transmit no light, and the light transmitted by solutions of less thickness is compound white light made up of the rays of two complementary beams, one having its centre in the yellow, and the other in the indigo of the spectrum.

Under certain circumstances, as described, nickel forms yellow solutions, and copper forms copper-red solutions, while under similar circumstances cobalt forms orange solutions.