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COLOUR AND CHEMICAL CONSTITUTION

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COLOUR AND CHEMICAL CONSTITUTION.

PART VIII.—FLUORESCENCE AND ITS LAWS.

BY JAMES MOIR, M.A., D.Sc., F.I.C.

While engaged in investigating the absorption-spectra of uranium compounds (see Part VII), I noticed that the green fluorescence which they mostly exhibit had a very definite emission-spectrum of 4 or 5 nearly equally spaced bands of about the same breadth as the bands (in the blue) of the absorption-spectrum. This phenomenon has been known for a long time in the case of uranium glass, but I think it is generally believed that all uranium compounds give the same fluorescent spectrum, which is not the case.

It is true that all aqueous uranium solutions, which by the way are devoid of fluorescence, if examined in a thick layer of dilute solution, give the same absorption-spectrum, this spectrum being due to the ion UO_2^{++} . The differences are only shown when there is *no* ionisation, *i. e.* in the solid state or in non-aqueous solution—and in such case there is generally a fluorescence.

The following are the positions of the centres of the bands in these emission-spectra of fluorescent uranium compounds:—

- (1) *Uranyl nitrate crystal*: $\lambda\lambda$ 560, 535, 510 and 485 (vague).
- (2) *Uranyl acetate crystal* (yellow): only one bright band, at about λ 525.
- (3) *Basic uranyl acetate* (orange): $\lambda\lambda$ 560 (vague), and 536 and 511.
- (4) *Autunite (calcium uranyl phosphate)*: $\lambda\lambda$ 575, 554, 529 and 508.
- (5) *Uranyl bisulphate* (in H_2SO_4): $\lambda\lambda$ 565, 541, 514 and 492.
- (6) *Uranyl metaphosphate* (in HPO_3 solid): $\lambda\lambda$ 590, 566, 542, 515 and 495.
- (7) *Uranyl sodium metaphosphate* (microcosmic bead): $\lambda\lambda$ 602, 562, 543 and 517.
- (8) *Solid uranyl chloride* had a fluorescence too faint to observe.

As will be seen on examining these figures, the bands are equally spaced or rhythmic: probably there are always five of them, but some are too faint to observe, and it is not always the same one in the order which is the brightest. It is therefore rather difficult to correlate them, but I have succeeded in finding a remarkable numerical relationship between the wavelength of any fluorescent band and that of the absorption-band which

(presumably) gave rise to it. For example, if we confine our attention to the band of second highest wave-length, we find that the fluorescent light has a wave-length which is 1.14 times the wave-length of the second line in the absorption-spectrum, and this figure holds for all the substances. For uranyl nitrate the fluorescent line is λ 535 and the absorption line λ 470; for basic uranyl acetate the respective figures are λ 536 and λ 471; for autunite the figures are λ 554 and λ 485; for uranyl bisulphate they are λ 541 and λ 475; and for the metaphosphates (acid and sodium) the ratios are 542/475 and 562/492. These ratios vary only between 1.139 and 1.142, which is purely experimental error.

Again, if we confine our attention to the first band in each substance, the constant ratio for all the substances is again met with, but this time it is 1.150: the particular cases are: uranium nitrate 560/486, uranium bisulphate 565/492, autunite 575/500, uranyl acid metaphosphate 566/492, the variation in the ratio being from 1.149 to 1.151.

For the third band there is again a constant ratio, the value of which is about 1.119, and for the fourth band, which is, however, not accurately observable, the value of the constant ratio is about 1.110.

The fact that these four ratios should themselves be so close together and yet be undoubtedly different for each of the four corresponding lines is in itself very remarkable. At first sight one would suppose that the ratio represents the ratio of two adjacent natural numbers, *e.g.* 8/7, on the supposition that the fluorescent light is the seventh harmonic of a fundamental of which the absorbed light is the eighth harmonic. As will be seen above, the fluorescence phenomenon is independent of the size of the molecule, the ratio being the same for all the substances. It may next be noted that the change in ratio from the fourth to the first line is about 1 part in 29, whereas the corresponding change in wave-length, *e.g.* 575 to 500 in autunite, is about 1 part in 7, so that it appears that the value of the ratio varies according to the fourth root of the fluorescent wave-length. Thus $1.15 \div 1.11 =$

1.036, whilst the value of $\sqrt[4]{\frac{575}{500}}$ is 1.036. Again, the values for the other

substances are: $\sqrt[4]{\frac{560}{486}} = 1.036$ (nitrate); $\sqrt[4]{\frac{565}{492}} = 1.035$ (bisulphate);

$\sqrt[4]{\frac{566}{492}} = 1.034$ (metaphosphate). It becomes thus possible to show that

any fluorescent line can be directly calculated from an observation of the position of any other fluorescent line along with an observation of the corresponding absorption line.

The equation $\frac{A_s}{A_t} = \left(\frac{F_s}{F_t}\right)^4$ holds true for all the lines, in which A_s and F_s are corresponding wave-lengths in the absorption and in the fluorescent

spectrum, and A_l and F_l the wave-lengths of the lowest band in the two spectra respectively. Thus in uranyl metaphosphate the lowest fluorescent band is at $\lambda 495 = F_l$. Now suppose that the *absorption* spectrum shows a band at $\lambda 460 = A_n$ and a last band at $\lambda 446 = A_l$. The value of $\frac{A_n}{A_l}$ is

1.031, and this, raised to the $4/3$ power, gives the value of $\frac{F_n}{F_l}$, viz. 1.042.

Hence F_n calculated is $515\frac{1}{2}$: the observed value was 515. Expressed in words, the equation means that the cube of the fluorescent wave-lengths varies as the fourth power of the absorption wave-lengths, or that the cube of the ratio of two fluorescent frequencies is equal to the fourth power of the ratio of the corresponding absorption frequencies. If we employ a constant to eliminate the necessity for an observation of the lowest wave-length the formula becomes:

$$F_n = 0.145 (A_n)^{\frac{4}{3}} \text{ (three figures only in wave-length reading).}$$

Thus if there is an absorption band at $\lambda 499$, $A_n = 499$, and F_n is $0.145 \times 499 \times 7.93 = 574$. This gives the central wave-length of the fluorescence. What the physical basis of this may be in terms of light-waves and periodic time of electrons I must leave to physicists to elucidate. Meanwhile I may point out that the ratio of fluorescent emission to absorbed wave-length is much the same amongst organic compounds, viz. about 1.15 for both fluorescein and rhodamine, so that the law appears to hold for many substances other than uranium compounds.