

XXVIII.—*The Form of Extinction Curves : Cobalt Nitrate Solutions.*

By THOMAS RALPH MERTON, B.Sc.(Oxon.).

IN emission spectra the distribution of intensity in spectral lines has been the subject of numerous investigations, and has in many cases been found to conform with definite laws. In the case of absorption spectra, however, no attempt appears to have been made to express the shape of extinction curves according to any law, largely, no doubt, on account of the large number of apparently anomalous shapes in which they occur. It has been shown by the

author (*Proc. Roy. Soc.*, 1912, A, **87**, 138) that the superposition of two or more extinction curves may account for the form of apparently complicated curves. It would seem, in fact, simpler to assume that all apparently complicated curves are in reality due to the superposition of curves of simple form than to attempt to express them by any mathematical laws.

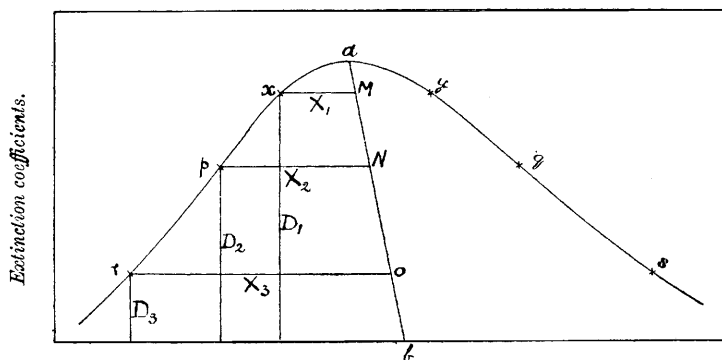
The object of the present investigation has been to find some solution which exhibits a single absorption band unaffected by the presence of other superposed bands, and to examine the form of the extinction curve.

An instance of this kind has been found to occur in the case of solutions of cobalt nitrate, which have a single absorption band in the visible spectrum.

The method of investigation and the apparatus used has been described in a previous communication (this vol., p. 124).

FIG. 1.

Wave-lengths.



The *D*-lines of a sodium flame were superposed on each absorption spectrum, and the wave-lengths were calculated by means of a carefully drawn interpolation curve. It was found that the standard density plate used showed slightly diminished density below wave-length 4100. As a precaution, no measurements were made below 4250. Kahlbaum's nickel-free cobalt nitrate was used. It was partly dehydrated over calcium chloride in a vacuum, and the amount of cobalt in it was estimated.

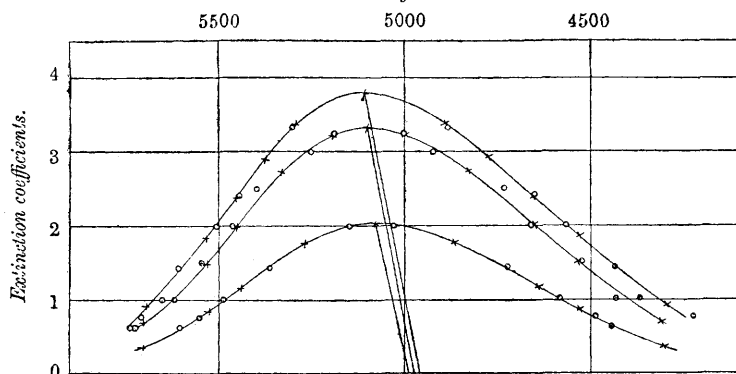
It has been found that the form of the absorption curve can be expressed within the limits of experimental error in a simple mathematical form. The manner in which this has been arrived at can best be understood by reference to Fig. 1. The curve given indicates the general form of the extinction curve of a solution of cobalt

nitrate. The curve is found to be symmetrical about the straight line ab , drawn from the maximum through the points M , N , and O , which are found by bisecting the distances $x y$, $p q$, and $r s$ (these being any points of equal extinction on opposite sides of the absorption band).

It has been found that the form of the curve about the line ab may be expressed by the formula $-\log y = c^2 x^2$, where y is any density (D_1 , D_2 , and D_3) relative to the density at the maximum, x the corresponding distance from the line ab (X_1 , X_2 , X_3), and c^2 a constant depending on the nature of the substance. This formula has been found to hold for cobalt nitrate solutions within the limits of experimental error.

In Fig. 2 are given curves of the extinctions of three aqueous

FIG. 2.
Wave-lengths.



solutions. The circles indicate the determined points, and the crosses the values calculated by the formula.

It will be seen that the points calculated are in good agreement with the values found. Attention must be drawn to the fact that the constant c^2 is not independent of the concentration, but becomes greater as the solution is diluted, that is to say, the band becomes narrower. The magnitude of this can be best appreciated by calculating the "half-widths" of the bands, that is to say, the values of x when $y = 0.5$. The concentrations, together with the values of c^2 , the half-widths, and extinction coefficients at the maximum, were as follows:

Concentration, grams of cobalt per litre (approximate).	c^2 .	Extinction coefficient (at maximum).	Half-width.
22	1.523	2.04	444
37	1.405	3.35	463
42	1.262	3.8	488

(For convenience of calculation the values of x were measured in units of 1000 Å.U.)

The fact that the solution does not obey Beer's law is indicated by the fact that c^2 alters with the concentration, and also that the lines about which the curves are symmetrical do not meet at a common point at zero extinction. The points at which these lines cut the axis are, of course, obtained by extrapolation, and in consequence great weight must not be attached to their exact values, but attention may be drawn to the fact that the point appears to move towards the violet with increasing concentration, whilst the wave-length of the maximum moves towards the red.

Measurements of the extinction curves in alcohol solutions indicate that the formula gives as good results in the solvent as in aqueous solutions. It may be pointed out that the expression is not entirely empirical, this form of equation having been used by Michelson and others to express the distribution of light in emission lines. No explanation, however, can be offered for the inclination of the line about which the curve is symmetrical. It seems very probable that curves of this type will be found for many other substances, and it is suggested that this may be the normal form of a single absorption band, most bands being due to the superposition of curves of this type.

Some evidence at least may be looked for in the changes of the constants of the equation in different solvents, and with changes of temperature, and experiments in this direction are now in progress.

25, GILBERT STREET,
LONDON, W.
